PHYSICAL AND GEOCHEMICAL CHARACTERISATION OF CANAL SEDIMENTS IN THE BLACK COUNTRY, WEST MIDLANDS.

A thesis presented for the degree of

Doctor of Philosophy

by

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A thesis submitted in fulfilment of the requirements of the University of Wolverhampton for the award of the degree of Doctor of Philosophy (Ph.D.)

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ABSTRACT

Potentially harmful elements (PHEs) have been researched in a wide variety of disciplines, including pedology, chemistry, pollution science and medicine. Within the scientific community, emphasis has usually been placed on the toxic elements, such as cadmium, chromium, lead and arsenic, but rarely has there been consideration of interactions between PHEs, the sediment matrix and processes occurring in the sediments. Dredging of canals is needed for navigability purposes and consequently testing of dredged sediments (to assess whether sediments are hazardous) and landfilling can be costly for British Waterways facing constantly changing regulations and reduction in government grants. PHE mobility and availability in canal sediments can be affected by oxygen availability, pH and Redox. Remediation is thus becoming a priority for British Waterways to limit their operational costs. Zeolites, a type of remediation tool, have been widely studied in the past 30 years due to their attractive properties, such as molecular-sieving, high cation exchange capacities and their affinity for PHEs. The pilot study to investigate the efficiency of the clinoptilolite showed that there was a concentration difference between PHEs adsorbed by the clinoptilolite and the PHE concentration lost from the sediments from three sites in the West Midlands. Thorough characterisation of the sediments was needed to understand the speciation of the PHEs and the secondary processes occurring in the sediments. The different components of the sediments were analysed using various analytical methods, such as X-Ray Fluorescence spectroscopy (XRF), particle size and X-ray Diffraction (XRD) for the solid-inorganic phase, Ion Chromatography (IC) and Inductively Coupled Plasma-Optical Emissions Spectroscopy (ICP-OES) for the liquid phase (pore water), Gas Chromatography-Mass Spectrometry (GC-MS) and organic loss on ignition for the organic phase, pH and Redox for the electrochemistry of the sediments and Scanning Electron Microscope with Energy Dispersive X-Ray analysis (SEM-EDX) for microscopy and imaging. The British Geological Survey (BGS) sequential extraction method was used to investigate the different phases in the sediments. pH remained near neutral for all three sites and Redox remained anoxic. Organic contents for all three sites were around 30% and contained most of the polycyclic aromatic hydrocarbons considered hazardous. Pore water showed only high concentrations of sulphates but low concentrations of PHEs, suggesting PHEs were not mobile. Sequential extraction confirmed the other results showing that PHEs were mainly associated with stable phases, such as iron and manganese oxides or sulphides. The results have been taken into consideration to design a new remediation strategy to maximise efficiency of the zeolite.

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DEDICATION

Finally, I cannot find the right words to express my utmost gratitude to my mother, Viga and father, Govind, who have supported me morally and financially throughout my life and my studies and who gave up everything to move to England and support me. My sister, Yovani, who has always believed in me and supported me.

This thesis is dedicated to my

Mother & Father,

Viga & Govind

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List of Abbreviations

BCN	Birmingham Canal Navigations
BW	British Waterways
CIRIA	Construction Industry Research and Information Association
CISED	Chemometric Identification of Substrates and Element Distribution
DEFRA	Department of Environment, Food and Rural Affairs
EDX	Energy Dispersive X-Ray
GC-MS	Gas Chromatography Mass Spectrometry
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emissions Spectroscopy
PAH	Polycyclic Aromatic Hydrocarbons
PFA	Pulverised Fuel Ash
PHE	Potentially Harmful Element
Redox	Oxidation/Reduction Potential
SEM	Scanning Electron Microscope
SEQ-EXT	Sequential Extraction
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence spectroscopy
ICRCL	Interdepartmental Committee on the Redevelopment of Contaminated Land
Ag	Silver
Al	Aluminium
As	Arsenic
Br	Bromium
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
K	Potassium
Mg	Magnesium
Mn	Manganese
Na	Sodium
Ni	Nickel
Pb	Lead
S	Sulphur
Sn	Tin
Ti	Titanium
Zn	Zinc

INTRODUCTION
CHAPTER 1

"He that would have the fruit must climb the tree"- Thomas Fuller

CHAPTER 1

INTRODUCTION

1.1 WHY DREDGE SEDIMENTS?

It is becoming more and more important to study dredged sediments as environmental regulations, contaminated land and disposal of industrial waste are becoming increasingly challenging for British Waterways. Canals in the United Kingdom (UK) and European Union (EU) are crucial for the leisure and manufacturing industries, and need to be maintained for navigability; at present dredging is the only option to maintain canals and navigable waterways at a suitable operational depth.

Sedimentation is a cumulative process in canals due to erosion, the deliberate and non-deliberate dumping of waste and urban and industrial run-off, as shown in Figure 1. It thus follows that sediments in canals may act as sinks for pollutants and may potentially pose a threat to water quality.

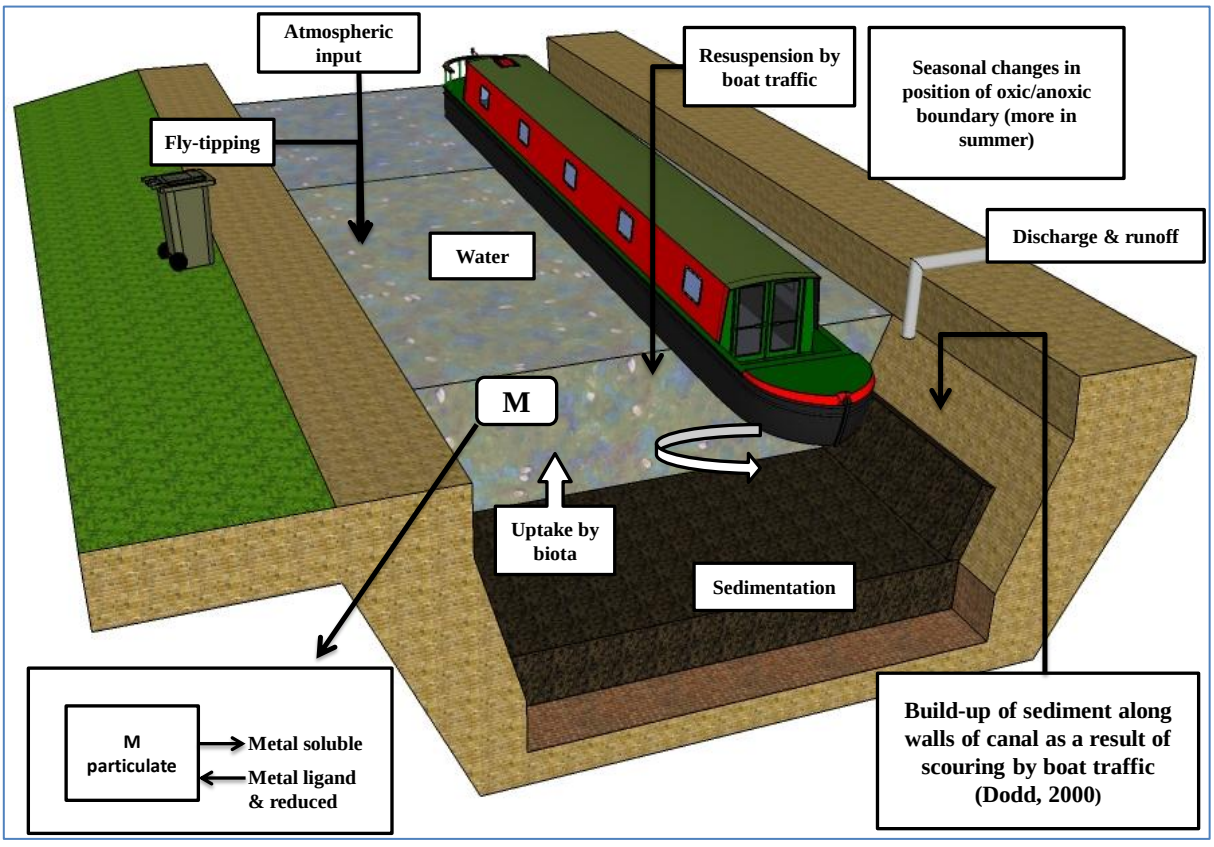


Figure 1: Processes involved in sedimentation in canals.

British Waterways are responsible for the maintenance of the canal network (Figure 2) in the UK, and about 7-10 million tonnes of sediments are dredged annually at a cost of £15-20

million (CIRIA, 1997). For example, the River Lee navigation runs through the London Olympic 2012 site. Here sediments have been dredged to regenerate the area, to improve habitat for wildlife and plants creating a green corridor running through the heart of the site and to re-establish the canals as the major transport network for the construction of the Olympic site. The dredging of the River Lee navigation through the Olympic site started in May 2009 (as shown on Plate 1), a 2.2 km stretch of the canal removing more than 30 thousand tonnes of sediments and waste, including shopping trolleys, tyres and a few motor cars (which can be a serious hazard to navigation) according to the authorities (Google Images, 2010; Olympic Delivery Authority Press Office, 2009).

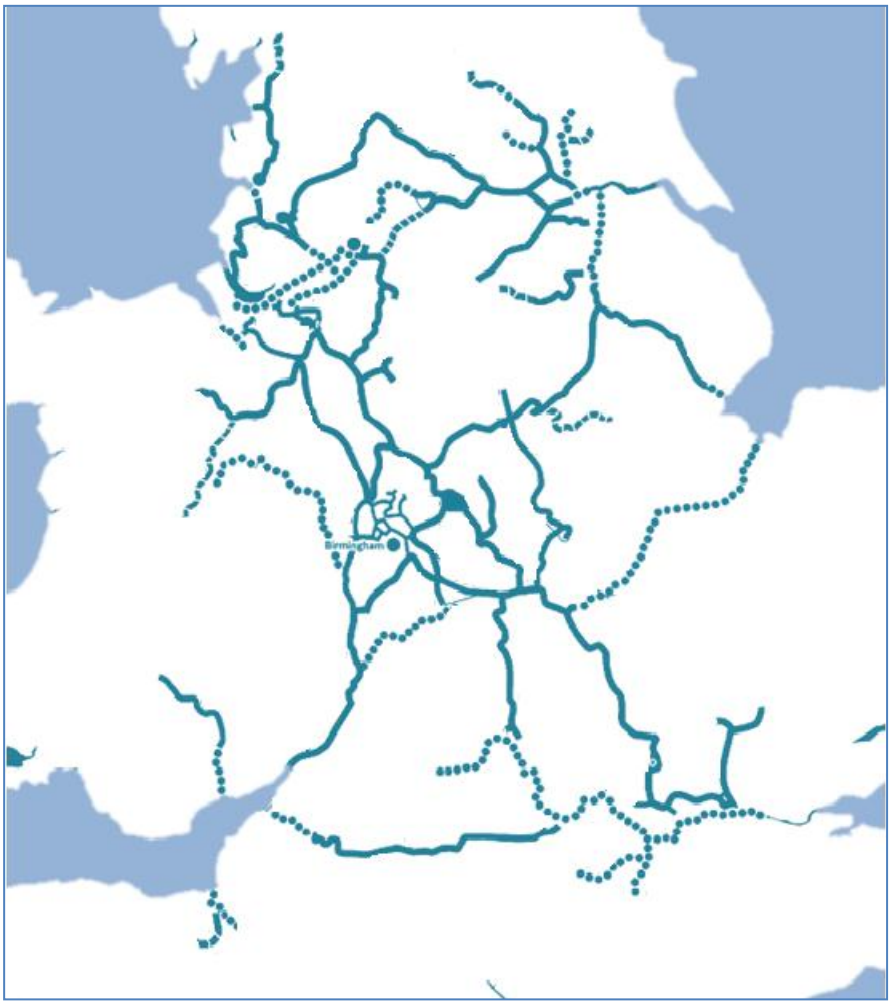


Figure 2: Map showing major navigable waterways in England and Wales, canals represented by lines, rivers represented by dots (British Waterways Leisure Dept., 2008).

Plate 1: Olympic site dredging a) initial stages of dredging, b) and c) sediments being loaded on barges, d) barge used by British Waterways for transporting dredged sediments and e) car being removed from the canal.

Canals are artificial channels built for the transportation of water, or to have water as a medium of transportation. The earliest canals built were in Mesopotamia and Indus Valley around 4000 BC and Egypt 2332-2283 BC and were mainly for irrigation purposes (De MareÌ, 1950). The first canal in Europe was built in Milan in 1127 which allowed development of commerce, transport and agriculture (Hadfield, 1986). This was followed by the development of canals in other European countries, such as Germany, France and The Netherlands. Canal building ideas and technology diffused into England from France which was visited by the Duke of Bridgewater and many English noblemen (De MareÌ, 1950).

1.2.1 Canals in the UK

Many scientific discoveries in the 18th Century brought about the Industrial Revolution. Rivers and navigable waterways had already been improved or extended, but artificial waterways as such had yet to be constructed (De MareÌ, 1950). Expanding domestic trade resulted in increasing pressure on the improvement of internal transport (Staffordshire Education, 1978). The pioneers who initiated the development of waterways were the Darby family who owned the Coalbrookdale Ironworks near the River Severn in the Ironbridge Gorge, Shropshire. Although the birthplace of canals was Manchester (Rolt, 1985), the growing coal and iron industries in Birmingham and Staffordshire soon became the hub of canal navigation. The Birmingham Canal Navigations (BCN) was originally created in 1767 to transport raw materials and end-products wherever they were needed in the West Midlands area. The BCN network was one of the largest in the UK with 255 kilometres of canals (500 arms and wharves). The BCN soon became an influential company in the West Midlands mainly because it was well established before the French Wars, which brought about inflation and hindered other canal development in other areas of England. From the BCN, many branches started growing, making the intricate network known today (Rolt, 1985).

The arrival of the rail network in the West Midlands, in the mid-nineteenth Century, followed by the improvement of the road networks brought new means of transport for goods and thus many canal sections were closed down. Many BCN carriers were retired with the decline of the collieries (coal being the main product transported). Between 1930-1960, heavy industrial trade had stopped and canals were used mainly by the tar companies trading between the Midlands and the North. A long period of neglect followed and the remaining 160 kilometres of the BCN canal system (Figure 3) was subjected to weed invasion and fly-tipping (Staffordshire Education, 1978).

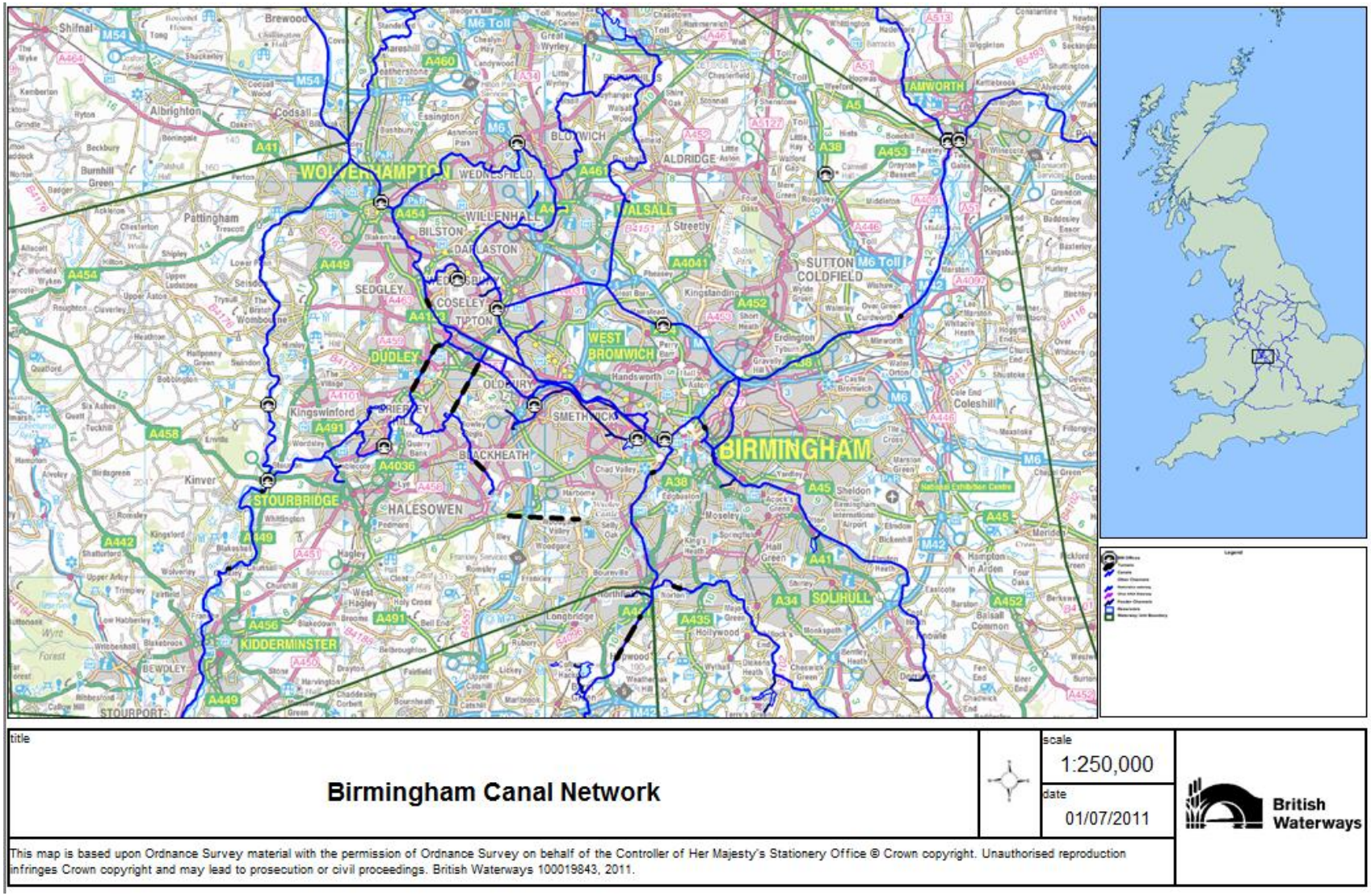


Figure 3: Birmingham Canal Navigations (BCN) network, courtesy of British Waterways.

1.2.2 Changing uses of canals

The fate of the BCN and other navigable waterways has changed in the latter part of the 20th Century from industrial purposes to recreational and leisure purposes (1960s onwards) and canal banks are being redeveloped nationwide for housing purposes (Wolverhampton City Council, 2006). Some 94% of the UK's population think that canals are 'an important part of the nation's heritage' and are among the most accessible and inexpensive resources for recreational activities, such as jogging, cycling and fishing (British Waterways, 2007). There were more than 28 million visitors in 2006 alone with a record 30,905 boats licensed on the national network. The waterways give travellers unique access to unspoiled countryside, keeping in mind sustainable tourism and national heritage and the legacy of the industrial revolution in Britain (Rodrigues, 2010).

Canals are now used mainly for recreational purposes but, according to Inland Navigation Europe (INE), these waterways could revert to their original use, to cater for the logistical requirements and the sustainable development of the larger 28 members European Union (INE, 2010). The European waterways network has more than 35,000 km of river and canals transporting over 485 million tonnes of international freight each year (INE, 2010). Several member state transport ministers have agreed to support the development of this network. In the UK, the Cotswold canals benefitted from a €4.8 million grant for the regeneration of the canal system under this scheme.

1.3 BRITISH WATERWAYS

British Waterways (BW) is a state-owned company funded by the Department of the Environment, Food and Rural Affairs (DEFRA) and various smaller grants. The company is responsible for keeping the waterways navigable, maintaining the paths and making the canals accessible for the new users, such as cyclists and walkers (British Waterways Leisure Dept, 2008). BW has undertaken several research projects to assess the quality of water and sediments all over the canal system and has made amendments where necessary, in accordance with the Water Framework Directive (Beckwith and Smith, 1999; Beckwith, 2007a). BW is responsible for about 1000 wildlife conservation sites and over 60 sites of special scientific interest. Seventeen of these sites are of European Importance recognised as Natura 2000 sites (British Waterways, 1999) which accounts for 482 kilometres of conservation areas. There are also over 2600 listed structures making British Waterways the third largest estate of listed structures in the UK.

Regulations on waste and environmental protection add to the complexity and cost of BW's task to dispose of the dredged material. It is now becoming a priority to investigate the dredged sediments in order to assess the potential risk they pose to the environment and to human health. There is also a need for an increased understanding of contaminant chemistry for both the newly dredged sediments and for previously dredged sediments exempt from licensing (Beckwith, 2007a; Beckwith, 2007b; Beckwith and Smith, 1999). BW spent a record £3.9 million on dredging alone in 2009/2010 (an 86% increase compared to £2.1 million in 2008/2009) which is a considerable amount of money when taking into consideration the effects of the financial crisis (British Waterways, 2010a). Moreover, the Government grants have been reduced to £70.2 million, whilst the total expenditure for British Waterways has increased to £192.4 million (British Waterways, 2010a).

1.4 REGULATIONS

There has been a gradual and important change in the status of dredged canal sediments in the past twenty years. Dredged sediments have stayed the same, but their status according to various directives and regulations have changed. Initially, The Control of Pollution Act (1974) introduced the term 'controlled waste' which meant that disposal sites needed licensing and waste had to be 'harmless' to the environment (Stephens, 2001; Dept. of the Environment, 1990). Later in 1988, the Collection and Disposal of Waste Regulations (1988) classified dredgings as industrial waste, falling in the controlled waste category. The Environment Protection Act was introduced in 1990 with one main implication for waste disposal; Duty of Care (DEFRA, 2006). Sections 34(1)(b) and (c) state that it is the responsibility of the producer (British Waterways) to prevent the escape of waste from the producer's control and to ensure that the transfer and the disposal of the waste is made by an authorised person. The Environment Protection Act (1990) resulted in the Waste Management Licensing Regulation (1994). This introduced formal documentation on the type, origin and destination of waste to be in the possession of the carrier during transfer. This meant that dredgings had to be characterised as a pre-requisite for disposal. The majority of dredged sediments in the UK were suitable for disposal under exemption from the Waste Management Licensing Regulations (1994). The three categories of dredged sediments were assigned Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) trigger values and sediments in category C[1] for example, exceeded ICRCL

[1] Categories O,A,B and C; Class A: sediments suitable for disposal to agricultural land/adjacent land, Class B: sediments suitable for disposal under exemption from the Waste Management Licensing Regulations (1994). Class C: sediments need further investigation before being disposed.

threshold for parameter other than zinc, nickel, copper, boron, phenol and sulphide and therefore needed further investigation before disposal. The consultation for this regulation was lengthy and BW with other stakeholders formed a group facilitated by the Construction Industry Research & Information Association (CIRIA) who published a guidance manual, 'the guidance on the disposal of dredged material to land', after the regulations were published (Beckwith *et al.*, 2001).

In the meantime, the European Hazardous Waste Directive (91/689/EC) focused on hazardous waste and provided an effective system of control for waste that is difficult to handle. Directive (91/689/EC) defined a complete list of waste whether hazardous or not and a classification according to the degree of the hazard expected. In the UK, the implementation of Directive (91/689/EC) resulted in the Special Waste Regulation (1996).

Another important directive from the European Union is the Landfill Directive (1999/31/EC). In general terms, this aims at reducing the volume of wastes going to landfill. More significantly, it sets out to ban liquid wastes from landfills in order to reduce contamination of groundwater, aquifers and soils through leaching. Since the Landfill Directive gives no clear definition of liquid wastes, DEFRA gave a definition to be used by regulators in the UK. The definition of a liquid waste is: "any waste that near instantaneously flows into an indentation void in the surface of the waste or any waste containing free-drainage liquid substances in excess of 250 litres or 10% whichever represents the lesser amount" (DEFRA, 2009). Sediments are considered liquid when they are dredged and fail the stick test. The stick test is the initial test carried out by BW to assess the physical characteristics of dredged sediments. A stick is probed into the sediment and removed. If the structure collapses around the hole, the dredged sediments fail the stick test and are thus considered liquid (Proffitt and Beckwith, 2007). Even in this case, BW has clearly emphasised to DEFRA that more scientific methods had to be developed as the definition was not suitable for dredged sediments (Beckwith and Smith, 1999; Great Britain Parliament- House of Commons *et al.*, 2007). The Landfill Directive was implemented in the UK by the Landfill Regulations (2002). This brought about the Waste Classification Guidance WM2 in 2003. The fate of dredgings at this point was still unclear as sediments could be classified as 'hazardous' instead of 'special'. The introduction of the Hazardous Waste Regulations (2005) (Environment Agency, 2006) changed the status of dredged sediments to 'hazardous,' which meant a dramatic change in the cost of disposal for BW as dredged sediments had to be disposed in hazardous waste landfills (Great Britain Parliament- House of Commons *et al.*, 2007).

The Water Framework Directive (2000) also has an impact on the management of the canals, as this piece of regulation is mainly related to the water quality and must be implemented by 2015. Articles 3 and 9 are particularly important as they formalised the 'polluter pays' principle and formally nominated an organisation for the management of the water body. In the UK, BW was nominated as the management body (Commission of the European Communities, 2000).

In 2010, the two regulations, the Pollution Prevention Control (PPC) and the Waste Management Licensing Regulations (WML) were combined to form the Environmental Permitting Regulations (2010), which includes water discharges, radioactive substances and provision for a number of directives, for example the Mining Waste Directive (2006/21/EC).

Finally, the Waste (England and Wales) Regulations (2011), puts an exemption into place for dredged material. These Regulations do not apply in relation to waste which is excluded from the scope of the Waste Framework Directive (2006/12/EC) by Article 2(1), (2) or (3) of that Directive.

1.5 CLASSIFICATION OF DREDGED SEDIMENTS

1.5.1 UK guidance for contaminated land

In addition to the regulations outlined in Section 1.4, the British Government provides guidance for the risk assessment of contaminated sediments. Much of the previous research had considered the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) trigger concentrations and established standards but, since then, this has been considered outdated (King *et al.*, 2006). It has not been replaced by any regulations whether in the UK or in Europe. The Environment Agency in partnership with DEFRA has introduced Soil Guideline Values (SGV) which now includes hazard to human health (Dickinson, 2000), but this takes into consideration various biological parameters especially for humans. Thus, a high concentration value of a specific heavy metal does not necessarily mean that it could be hazardous. The SGVs are derived from the Contaminated Land Exposure Assessment (CLEA) model which assess and generates models for different land-uses. The CLEA model involves various parameters and models exposure (Environment Agency, 2005) and was derived from the 1990 Environmental Protection Act Part IIA. The CLEA model determines the potential risk posed by different contaminants based on the Hazard-Pathway-Receptor concept introduced by the Environment Act (1995) (DEFRA and Environment Agency, 2002). Another important document produced by the Environment Agency and DEFRA are

the toxicology (TOX) reports, which details the derivation of the health criteria values for the PHE. It works in conjunction with the SGV values. The SGV values can be used as reference concentrations (Environment Agency, 2002) but are not as straightforward as ICRCL trigger values. The SGVs provide a more scientific approach compared to the ICRCL values, as they are guideline values for 'intervention' although based on total amount of contaminant present instead of bioavailable amounts (Environment Agency, 2002).

This system was mainly used for redevelopment of land with *in situ* contamination and not designed specifically for dredged sediments (Challinor and John, 1997). This system has now been superseded by the CLEA guideline values, which take into consideration risk assessment, specific age and sex exposure assessments and contaminated land types. CLEA is a modelling system which is constantly being updated with risk assessments for different pollutants. However, it cannot be used *in situ* and to assess sites where dredged sediments have been disposed and thus does not assess the risk of the sediments before any potential contamination occurs.

1.5.2 British Waterways Classification Scheme for dredged sediments

BW developed a classification scheme in 1992 when a national sediment sampling strategy scheme was undertaken, producing a "national overview of dredging quality" for navigable waterways in the UK. Over 1000 samples were collected from various canal sites around the UK. This was carried out to facilitate classification of the dredged material and to help with exemptions for bank side disposal. Table 1 shows the characterisation result, which were reviewed in 2009 by the Environment Agency. The Environment Agency also agreed to consider the BW report, "Characterisation guidance for BW sediments" to be adequate for classification of dredged materials based on initial study by BW. The document details classification of dredged material and meets the requirements of the current version of the technical guidance WM2 (version 2.3) of the Waste Regulations (2011). The information from this document also provides guidance on whether to consider the dredged material hazardous or non-hazardous (British Waterways, 2010b).

The Bankside Screening Values (BSV) in Table 1 have been developed considering the screening values in place at the time, for example, the CLEA SGVs, the Dutch Intervention Values and Contaminated Land Report (British Waterways, 2010b).

Table 1: Bank side screening values for dredged sediments (British Waterways, 2010b)

	Bank side screening Value (mg/kg)*	Note:
Arsenic	20	Soil guideline values (SGVs)
Cadmium	30	
Chromium	200	
Lead	450	
Nickel	75	
Copper	1300	Hybrid of phytotoxicity & human health hazard values
Zinc	3000	
Total PAH	40	Dutch Intervention Values
pH	5<X<9	note: pH unit not mg/kg
* No land in agricultural use/ not owned by BW should be considered to be 'bank side'.		

Sediment contaminant concentration below the BSVs did not warrant further risk assessment, whereas contaminants above the BSVs required further consideration of the potential pollutant linkages. Exceeding these BSVs did not necessarily mean that the sediment be remediated.

1.5.3 Onland disposal

Once dredged, the canal sediments are usually spread to land and left to dry (for e.g., agricultural land). Pollution of nearby water courses is prevented by bunding in places to prevent run-off from sediments. The physical characteristics of the sediments are determined by their mineralogy and plasticity index (Brown *et al.*, 1980). The sediments are mainly fine minerals and are saturated with water. Thus the primary concern for the authorities is dealing with the water and to initiate the drying process before onland disposal can be undertaken. The chemical properties of the dredged material are strongly dependent on pH and Redox changes (Khalid *et al.*, 1977).

Waste is defined as a substance or object, which the producer or the person in possession of it discards, or intends to discard, or is required to discard (Challinor and John, 1997). The disposal of the waste material has to be licensed, except in some cases where the activity is deemed to be low risk and exempt from a Waste Management License (superseded by environmental resource permit). However, the exemption does not apply if the activity

involves hazardous waste, as defined by the Special Waste Regulations (1996) which was superseded by the Hazardous Waste Regulations (2005). Dredgings may be disposed of in three different ways without licensing; spread onto agricultural land, used in land reclamation and deposited on banks or towpaths. Conditions are attached for each type of disposal. The dredged sediments have to be less than 5000 tonnes (wet mass) per hectare per year and have to benefit agricultural or ecological improvement when spreading on agricultural land. When used for land reclamation, no more than 20,000 tonnes of dredged sediments can be spread per hectare of land and if deposited on banks or towpaths, the amount of dredged sediments deposited cannot exceed 50 cubic metres of dredgings per metre length of bank or towpath as outlined in the Environment Agency document D1, Deposit of dredgings from inland water (Challinor and John, 1997; Environment Agency, 2011). Regulations regarding canal sediments (and their disposal) have been discussed in Section 1.4. Canal sediments contain sometimes high concentrations of Potentially Harmful Elements (PHE) and other organic contaminants, such as Polycyclic Aromatic Hydrocarbons (PAH), and are considered as hazardous waste (Beckwith and Smith, 1999).

1.6 PROJECT RATIONALE

Industries are considering new transportation methods to reduce their costs. Using navigable waterways instead of road and air transport would reduce their carbon footprint, especially for trade in Europe (INE, 2010). This can be achieved using the already existing canal network, provided they are wide and deep enough for navigation (dredged regularly for commercial navigation). This illustrates how important new ways of disposing of the sediments and remediation or recycling have become. The rising cost of disposal of dredged material and legislation make it increasingly difficult for British Waterways to send dredged material to landfills. More money is now being used for research on remediation (Ferrarese *et al.*, 2008; Mulligan *et al.*, 2001; Perelo, 2010; Querol *et al.*, 2006) or solidification/stabilisation technologies (Agostini *et al.*, 2007; Demars *et al.*, 1995; Fuentes *et al.*, 2004a; Mulligan *et al.*, 2001) so that landfills can accept the waste in the future, whilst reducing the amount of waste produced. The remediated waste can afterwards be reassessed and thus be considered in a different category of waste resulting in lower costs of disposal. Characterisation of the sediments means that a more efficient remediation strategy can be developed. The dredged sediments are often contaminated with sometimes elevated concentrations of PHEs and characterising the sediments helps assessing the risk to human health and the ecology of canals in general. Understanding the (im)mobility of PHEs in dredged sediments will help

BW and the EA to reassess the status of sediments and the risks to human health and the environment. There is also a need for an increased understanding of contaminant chemistry for both the new dredged sediments and for previously dredged sediments exempt from licensing (Beckwith, 2007b; Beckwith, 2007c; Beckwith and Smith, 1999).

1.7 AIMS AND OBJECTIVES

The aims of the objectives of this research are:

Aim 1: Geochemical and geophysical characterisation of canal sediment (form, size, oxidation state, pH, supernatant and behaviour).

Objectives:

1. To conduct an extensive literature review on PHE and the way they behave in sediments and under different oxidation states and environmental conditions.
2. To devise a sampling strategy for areas identified in the West Midlands that have historically been extensively used for heavy industrial purposes and are known to be contaminated with hazardous materials, but have been subjected to little or no historic dredging.
3. To perform laboratory experiments including XRF, XRD, IC, ICP-OES, SEM-EDX, particle size, organic loss on ignition, and sequential extraction to thoroughly characterise the sediments and to determine the state in which the PHE occur in these sediments (i.e. form, shape and compound state).

Aim 2: To model behaviour of PHE in canal sediments.

Objectives:

1. To collate data from different geochemical analyses to model behaviour of canal sediments and PHE mobility and availability. Elemental concentration in sediments analysed by XRF and SEM-EDX, elemental concentration in pore water by ICP, ionic concentrations using IC, different metal compounds bound to specific fractions analysed by sequential extraction and the organics by GC-MS and dichromate tests all put together will give a detailed mapping of PHE and their behaviour in the sediments.

Aim 3: Develop a remediation strategy for canal sediments (and potentially other contaminated sediments) and to assess the effectiveness of zeolites and pulverised fuel ash (PFA) for remediation of canal sediment.

Objectives:

1. To carry out an extensive literature review on legislation concerning disposal of canal sediments.
2. To use characterisation results to map and model behaviour of PHEs in sediments and consequently design the remediation setups appropriately.
3. To formulate and design a laboratory experiment in order to monitor changes occurring within sediments and water with a combination of zeolites with voile mats and A4 size trays. Various combinations of clinoptilolite, chabazite, phillipsite and Pulverised Fuel Ash (PFA) will be used to assess their abilities to absorb water and PHEs and simultaneously stabilising the sediments
4. To design and formulate a remediation strategy for canal sediments and potentially other contaminated sediments using zeolites and PFA, on a small scale and medium-scale basis.
5. To carry out an extensive literature review on zeolites and their current use and PFAs as stabilisers.
6. To review the efficiency, efficacy and viability of zeolites as a remediation tool.

1.8 THESIS OVERVIEW

Chapter 1 outlined the overall rationale for research and the scope of research undertaken. Chapter 2 reports the outcomes from an initial pilot study into the potential remediation of canal sediments using clinoptilolite (a type of zeolite) and PFA. Chapters 3 to 6 present a more focussed and detailed research strategy to understand processes not fully explained by the limited scope of the pilot study. Chapter 3 details a new literature review on the characterisation of canal sediments. Chapter 4 outlines the methodologies used for the characterisation experiments. Chapter 5 presents the main results from the experiments used in this research and a statistical treatment of the data. Chapter 6 introduces new discussion on the characterisation of the canal sediments and processes operating within the sediments that have an influence on the potential for successful remediation strategies. Chapter 7 contains an option for a new remediation strategy based on the data and findings in this research.

A PILOT STUDY INTO THE REMEDIATION OF CANAL SEDIMENTS

CHAPTER 2

"Curiosity is the wick in the candle of learning"- William Arthur Ward

CHAPTER 2

A PILOT STUDY INTO THE REMEDIATION OF CANAL SEDIMENTS

2.1 REMEDIATION

Remediation is concerned with the removal, containment or abatement of a hazardous substance from environmental media, such as soil, groundwater, sediment and surface water that may pose a health hazard or is detrimental to the wider environment (Nathaniel and Bardos, 2005). Remediation strategies and techniques have been influenced by environmental laws and European regulations over the past 20 years and most EU countries either adopt Best Available Technology (BAT) or Best Available Technology Not Entailing Excessive Cost (BATNEEC). Both BAT and BATNEEC are currently enshrined in the Integrated Pollution Prevention and Control (IPPC) Directive 2008/1/EC. With respect to contaminated land in England and Wales, governmental guidance recommends that BATNEEC principles be adopted along with Part IIA of the Environment Protection Act (1990), which deals with contaminated land, rather than BAT (Emmott and Haigh, 1996). The end-use of a site often dictates the permitted levels of organic and inorganic soil composition and so it follows that economic constraints are often just as influential as remediation technologies (McGillivray, 2009).

There are various remediation techniques that have been developed over the years for various media. Although some of them might be very effective, cost remains one of the main factors influencing their potential use as a remediation tool. Remediation can be achieved by various methods either *in situ* or *ex situ*. *In situ* remediation techniques include capping, amendments and phytoremediation. *Ex situ* remediation techniques include washing, incineration, immobilisation using bacteria or amendments and flotation. Both *in situ* and *ex situ* techniques can be very expensive and not always suitable for canal sediments. In addition, although they are meant to reduce the impacts of the contaminants on the environment, many of these remediation techniques are not sustainable (Peng *et al.*, 2009) as they still produce waste or are not economical. *In situ* remediation methods are inappropriate for canal sediments as many canals are required for navigation, but remediation can be achieved by phytoremediation technologies (Ke *et al.*, 2003; King *et al.*, 2006; Querol *et al.*, 2006; Wang *et al.*, 2007) at the edges of canals where water depth is shallow and where navigation is not interrupted (Perelo, 2010).

2.1.1 Zeolites as a remediation tool

Remediation of the environment is an important concept nowadays and has been achieved using various methods, such as chemical precipitation, membrane filtration, ion exchange, absorption and adsorption. Research on low cost sorbents has been undertaken on lignin, zeolites, clays, fly ash, moss, modified wood, chitosan and bark (Bailey *et al.*, 1999; Colella, 1999; Babel and Kurniawan, 2003). It has been reported that zeolites remain one of the cheapest and most effective sorbents when considering PHEs (Babel and Kurniawan, 2003; Colella, 1999). Since zeolites have proven to be effective in heavy metal absorption (Cincotti *et al.*, 2006; Ouki and Kavannagh, 1997; Wang *et al.*, 2006) and is economical compared to other absorbents (Colella, 1999), this research will investigate zeolites as a potential remediation tool for dredged canal sediments.

2.2 ZEOLITES

Zeolites are a microporous, well defined class of crystalline aluminosilicate minerals. They occur naturally as minerals and contain silicon (Si), aluminium (Al) and oxygen (O) in the framework with cations, water and other molecules within their pores (Barrer, 1978; Dyer, 1988; Ribeiro *et al.*, 1984). The molecules have enough freedom of movement to permit cation exchange and reversible dehydration. Zeolites belong to the class of minerals known as tectosilicates, *i.e.* they have a molecular structure consisting of a three-dimensional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordinate polyhedra linked by their corners (Dyer, 1988). These corners can be linked in different ways producing various different structures. There are about 130 known framework structures with Si and Al as the tetrahedral unit. The isomorphous substitution of Si^{4+} by Al^{3+} results in a net negative charge, which is compensated by alkali and alkaline-earth metal cations within the framework (Barrer, 1978; Gottardi and Galli, 1985).

Zeolites mostly occur in sedimentary and low-grade metamorphic rocks and are found at various locations in the United States, Japan, Cuba, Russia, Italy, Hungary, Bulgaria, South Africa and Mexico often in high quantities and purities. They are among the most abundant minerals species on Earth (Barrer, 1978).

2.2.1 Clinoptilolite

Clinoptilolite $[(Na,K,Ca)_{2\text{-}3}\ Al_3\ (Al,Si)_2\ Si_{13}\ O_{36.}12H_2O]$ is part of the zeolites family of heulandite (Sprynskyy *et al.*, 2006; Yilmaz *et al.*, 2007); a natural zeolite used mainly as chemical filters, absorption and water purification, due to a high volume of pore space, high

resistance to temperatures (≤450ºC compared to other heulandites minerals) and a neutral structure (Tschernich, 1992). Clinoptilolite forms as a devitrification product of volcanic glass tuff when the glass is in contact with saline waters. Clinoptilolite is a sheet silicate containing alternating eight and ten-sided rings with widely separated spaces, allowing cations to pass through the sheet spaces (Rozic *et al.*, 2000). This molecular sieve property has been widely studied in various fields, as it can be used to absorb or remove targeted molecules (Pitcher *et al.*, 2004). The crystals of clinoptilolite are blocky or tabular and more proportioned than other minerals from the heulandite family (Erdem *et al.*, 2004; Stylianou *et al.*, 2007). Clinoptilolite also has pozzolanic (Martinez-Ramirez *et al.*, 2006) or cementitious properties which is desirable when considering immobilization of PHEs (Yilmaz *et al.*, 2007).

2.2.2 Pulverised fuel ash (PFA)

PFA is a waste by-product of coal combustion in power plants and is produced in enormous quantities; around 115 million tonnes produced every year in Europe and USA alone (Querol *et al.*, 2002). PFA comprises mainly of SiO_2 and Al_2O_3 and is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of furnaces (Querol *et al.*, 2002). Disposal to landfills cost between £7-10/tonne in the UK (excluding landfill tax), which results in large cost of disposal for E-ON (one of the major energy providers in the UK) of about £917,000 annually (Tooth, 2007). It has been noted that PFA has similar pozzolanic properties (Bailey *et al.*, 1999; Jarvis and Brooks, 1996) to clinoptilolite and so may be used for the immobilisation and stabilisation of PHEs.

2.2.3 Synthesis of zeolites from pulverised fuel ash (PFA)

Zeolites can be synthesised from various raw materials with different conditions to suit requirements (Terzano *et al.*, 2005). PFA is one of the most popular starting materials due to its attractive properties. The problem of disposal is partly solved by using it to produce zeolites and thus the price of this raw material is very low compared to other sorbents (Colella, 1999; Bailey *et al.*, 1999). Since the preliminary research by Holler and Wirsching in 1985 (Querol *et al.*, 2002), many researchers have tried different parameters to synthesise zeolites from PFA. Most of these are based on the dissolution of Al-Si bearing fly ash phases with alkaline solutions (mainly NaOH and KOH solutions).

Querol *et al*. (2001), synthesised up to 13 zeolites from fly ash with temperatures ranging from 80-200 °C and using reaction times ranging from 3-48 hours when utilising potassium hydroxide (KOH) and NaOH solutions at different molarities. Wang *et al*. (2006) applied

hydrothermal treatment on PFA and found that using higher NaOH concentrations increased surface area of the particles and hence pore volume, due to transformation of PFA into zeolite.

Most of the research on PFA and synthesis to zeolites has shown that the parameters for high yields of zeolites remain temperature, pressure, concentration of solution and molar ratio of Si:Al (Juan *et al.*, 2007; Qu and Kelderman, 2001; Querol *et al.*, 2001). Increasing research is being conducted on the possibilities of synthesising zeolites in a simpler and cost-effective way and possibly on larger scale synthesis (Juan *et al.*, 2007; Ouki and Kavannagh, 1997).

2.3 RESEARCH ON ZEOLITES

In the past decade or so, there has been increased emphasis on zeolites and their potential applications in various fields. It has already been established that zeolites have beneficial properties and therefore widespread research on this new resource has been carried out, including removal of PHEs from soils, water and sediments.

2.3.1 Applications

Research on applications of zeolites has been carried out worldwide in many fields ranging from pharmaceutics, medicine, agriculture, catalysis and cracking of petroleum products among many others. For the purpose of this research, an analysis of research on the applications related to pollution and remediation using zeolites was considered. These can be divided into two broad categories: research involving aqueous solutions or wastewaters and research on soil or sediments.

One of the earliest studies on such applications was carried out by Blanchard *et al*. (1984), using natural clinoptilolite. The results showed that clinoptilolite is very efficient for the removal of lead (Pb) and ammonium ions from aqueous solutions. It has been well established that clinoptilolite has a high affinity for Pb (Blanchard *et al.*, 1984; Ouki *et al.*, 1994; Inglezakis *et al.*, 2002; Inglezakis *et al.*, 2003; Inglezakis *et al.*, 2007; Stylianou *et al.*, 2007; Babel and Kurniawan, 2003; Feng *et al.*, 2000). Selectivity of PHEs by zeolites has also been shown by Hui *et al*. (2005), who considered two adsorbents: zeolite 4A and fuel ash (treated and non-treated) with selectivity series Cu>Cr>Zn where Cu removal efficiency increased at higher pH. Inglezakis *et al.* (2003), also showed that the initial acidity of metal solutions determines selectivity of clinoptilolite in both single metal solution and multiple-metal cations solution, where cations can be replaced several times before equilibrium is reached.

Electroplating is one of the industrial processes that produces and contributes most to environmental pollution with toxic PHEs (Alvarez-Ayuso *et al.*, 2003). The main PHEs produced are cadmium (Cd), chromium (Cr), nickel (Ni), zinc (Zn) and copper (Cu). Natural clinoptilolite and NaP1 (synthetic zeolite) both showed preference for Cu and Cr and kyanite showed preference for Cu (mainly by precipitation of their hydroxides) and Ni (mainly by cation exchange processes) in research conducted by Ajmal *et al*. (2001). Similar research has been conducted on motorway stormwater (Pitcher *et al.*, 2004) in which PHEs such as vanadium (V), Cr, manganese (Mn), cobalt (Co), Ni, Cu, Zn, Cd and Pb were adsorbed by zeolites MAP, with an adsorption efficiency of ≥ 91%. Genc-Fuhrman *et al*. (2007) also studied PHEs in stormwater comparing 11 different sorbents and results showed that leaching of arsenic (As) and Cr limit their usage for some absorbents. Since zeolites are also thermally stable and resistant against radiation, they can also be used to treat radioactive wastewater. Clinoptilolite has proven to be very effective for removal of radioactive caesium, Ni, strontium and barium (Faghihian *et al.*, 1999). Zeolites can also be used to reduce total organic carbon (TOC), for example from printing ink (Metes *et al.*, 2004) and results showed that TOC was reduced by ≤95% together with removal of other PHEs. Research (Badillo-Almaraz *et al.*, 2003) undertaken on wastewater, showed that absorption of Zn (II) showed that Zn does not occupy the same sites as Pb in the zeolites and therefore there is no competition between the two divalent cations. Fine powdered zeolites which had higher removal efficiency, attributed to larger surface area favouring ion exchange compared to granulated clinoptilolite, can be used effectively as metal absorbers in industrial wastewaters, as shown by Ok *et al*. (2007). This research also tested adsorption of Pb at low pH and showed that adsorption increases with increasing pH from 1 to 4. Lower pH (<1) cannot be studied as the clinoptilolite structure breaks down, (dealumination), at pH this low (Inglezakis and Loizidou, 2007). Arsenic is removed from polluted water via ligand exchange where aluminol and silanol hydroxyl groups develop at the edges of zeolites (Shevade and Ford, 2004). The adsorption of As is very quick (about 15 minutes) and is most effective between pH 3 and 7. Lower Si:Al ratios also mean a greater concentration of aluminol surface groups resulting in greater capacities for As removal. Clinoptilolite was also used to remove silver (I) from aqueous solutions (Akgul *et al.*, 2006) where equilibrium was reached in 45 minutes at an optimum pH of 4.

Natural clinoptilolite also showed promising results for removal of Zn, Cu and Pb in aqueous solutions. Ion exchange can be accompanied by precipitation at higher initial concentration

(Peric *et al.*, 2004). The exchange capacities for Cu and Pb are also double compared to Zn. Cu follows ion-exchange and sorption mechanism in parallel and the selectivity series for natural clinoptilolite is in the order Pb > Zn > Cu, which is in accordance with other research (Stylianou *et al.*, 2007). Cr (III) and (VI) have been absorbed on bentonite and their thermodynamic calculation have shown that Cr (VI) absorption is favoured by higher temperature, whereas Cr (III) and silver (Ag) is less favoured by higher temperatures (Khan *et al.*, 1995). This shows how important speciation and characterisation are for any remediation research, as different forms of the same element can have different behaviours and thus hinder the removal efficiency of the zeolites.

Genc-Fuhrman *et al.* (2007), reported that PFA has a high affinity for Ni, Zn, Cu and Cd, but the high exchange capacities and affinity for these PHEs suggests that PFA may concurrently release other PHEs, e.g. As and Cr. High pH and high metals concentration also make fly ash more efficient at removing PHEs by precipitation rather than by ion exchange (Genc-Fuhrman *et al.*, 2007). It has been reported on the other hand that it can be efficient at removing Cr (VI) when mixed with wollastonite (1:1) and can be achieved at low pH. In the acidic pH range it can also effectively absorb mercury (Hg) (Babel and Kurniawan, 2003). The effectiveness of PFA can be increased with higher temperatures, but leaching remains a major drawback when considering this absorbent.

PFA has been used on its own in many sectors of the building industry, such as building roads, concrete and land fillings (Dirk, 1996). Although a large amount of PFA is being used, it only accounts for a very limited percentage of ash being produced. PFAs can be used on their own as adsorbents as mentioned above and they are very effective at adsorbing water and cations (although not as much as zeolites). Researchers (Babel and Kurniawan, 2003; Dirk, 1996) used the PFAs as they are, or pre-treated with sodium hydroxide (NaOH). Most research focuses on synthesis of PFAs into zeolites as it increases its efficiency to remove PHEs and water consequently increasing its market value considerably.

2.4 REMEDIATION PILOT STUDY

2.4.1 Preliminary trials by British Waterways

BW have undertaken trials for the remediation of canal sediments after dredging but faced many barriers. These barriers are cost, efficiency of remediation tool in both removing the contaminants from the sediments but also stabilising the sediments so they can be disposed in normal landfills or landfills owned by British Waterways (where only the ‘safe’ sediments are

disposed) (Beckwith and Smith, 1999; Beckwith, 2007b; Bromhead and Beckwith, 1994). Different methods have been used to stabilise the sediments such as 'the lime treatment' which is a treatment with similar properties to zeolites (British Waterways, 1998). The treatment was effective to stabilise the sediments rapidly turning it into a cementitious material but due to the volume required to treat the dredged sediments was not considered very effective. Moreover, this method still produced a large amount of waste and thus was not sustainable for British Waterways. Other trials on stabilisation and remediation of dredged sediments, called Project Aquarius, were undertaken in circular tanks to remediate the sediments (Beckwith, 2007b). These also proved to be inadequate for canal sediments as the contact time between the adsorbent and the sediment was reduced by the settlement of the sediments.

2.4.2 Methodology

The methodology for the pilot study was based on Stephens (2001) and Stephens *et al.* (2001a) where canal sediments were placed in plastic containers (dimensions 255 x 395 x 155mm) to investigate the geochemical changes which occur during drying and oxidation. However, in this research, zeolites were applied in order to study the potential benefits of zeolites as a remediation tool for canal sediments. Figure 4 shows the tanks used for the experiments and dimensions.

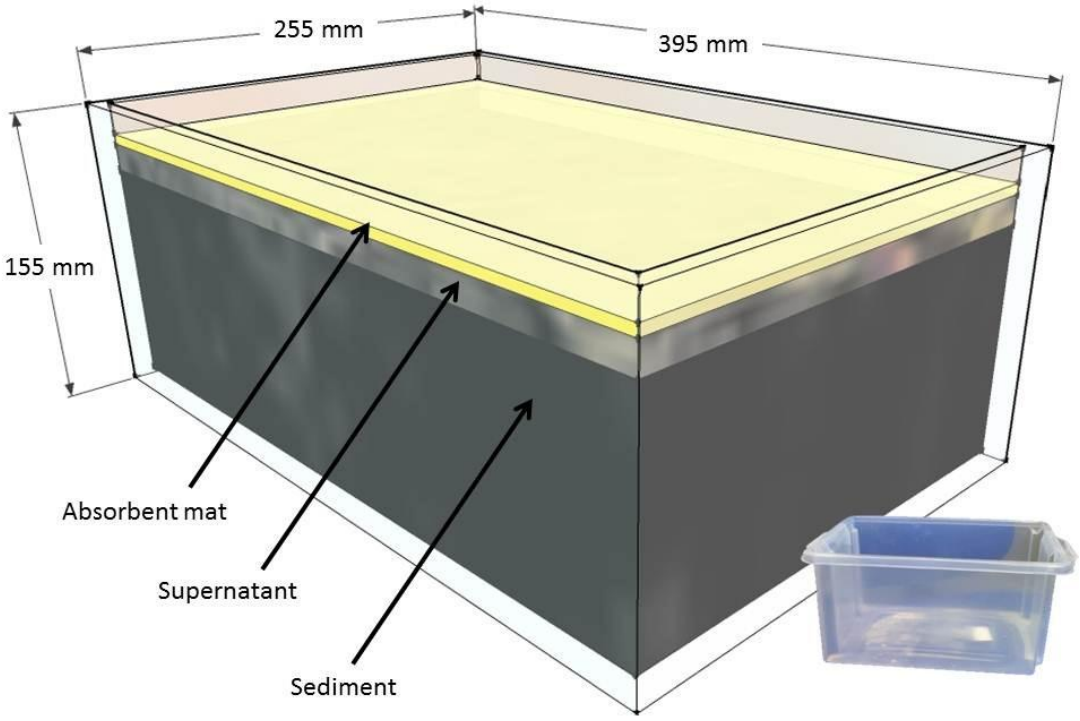


Figure 4: Remediation setup with zeolite mat on top (zeolite-cream colour in voile mats).

2.4.3 Experimental setups

The tanks used were identical to those plastic tanks used by Stephens *et al.* (2001a), which were the right size for laboratory experiments and conformed to health and safety regulations (weight) for laboratory experiments. Clinoptilolite and PFA mentioned in Section 2.2.1 and 2.2.2 were the main absorbents chosen for the remediation experiments in various combinations, concentrations (ratio of zeolite: sediment) and varying parameters such as pH and Redox. The pilot study started with three experiments to evaluate the efficiency of the zeolites and the experimental strategy overall. The first three experiments were:

i. Sediments with clinoptilolite.
ii. Sediments with PFA.
iii. Sediments with clinoptilolite and PFA (50:50).

For each experimental setup above, two tanks were used. The absorbent was placed in a pillow case made with voile and placed on top of the sediments in the tank. Eight samples were taken randomly (2 lines of 4 samples) from the sediments before the addition of the zeolite mat. After the experiment, another 8 samples were taken from the sediments and from the pillow case. The same number of samples was taken for the replicate box. The samples were then prepared for X-Ray Fluorescence analysis. Random samples were taken from various locations in the tank and homogenised. Because the PHEs behave differently with varying parameters, this sampling method has been favoured for the experimental setups.

2.4.4 X-Ray Fluorescence disc preparation

The sediment samples (three sections for each core) were oven dried in Al foil containers at 40 °C for 36 hours. Low temperatures were used so as not to alter the mineralogical properties of the samples (Reynolds *et al.*, 1989). Once thoroughly dried, the samples were crushed, using a pestle mortar, into a fine powder. A sieve (250 µm) was then used to separate the fine sediments from the coarser and any unwanted materials in the samples. This mesh size was used so that only clays, silts and very fine sands were in the final sample used for X-ray Fluorescence, as PHEs accumulate in smaller size sediments (Ellis and Mellor, 1995). Moreover, sieving avoids contamination of the sediments by foreign objects, such as iron fillings, thrown into the canal that could alter the results significantly. 8.50 g of the sediment powder was weighed accurate to two decimal places to which was added 1.50 g of Licowax to aid binding. The mixture was then shaken to make the final powder homogenous and was made into discs using a pressure of 12 tonnes. The discs were then removed from the

ram, bagged and labelled. The steel parts were again cleaned thoroughly with ethanol between each press to avoid contamination. In total, there were 15 discs for each tank which resulted in 150 discs for each site and 450 discs in total for the three sites.

2.4.5 Analysis using X-Ray Fluorescence Spectroscopy

X-Ray Fluorescence Spectroscopy (XRF) (Plate 2) has been widely used to analyse elemental concentrations in samples (Bianchini *et al.*, 2002; Huy *et al.*, 2003; Isaure *et al.*, 2002; Obiajunwa *et al.*, 2002; Reynolds *et al.*, 1989). X-rays are used to liberate electrons from the inner core (K or L orbital) of the element, making it unstable. When the element starts stabilising, electrons from the outer core of the atoms are transferred to the inner core (L to K or M to L orbital) but with a different wavelength (Jenkins, 1988). The wavelength is recognised by XRF and gives the specific element found in the sample. An element is identified by its characteristic wavelength (λ) or energy (E). The concentration of each element present in the sample is quantified by measuring the intensity (I) of the characteristic emissions

XRF has the advantage of being non-destructive, time and cost-effective and covers a wide range of the periodic table (except elements with atomic weight less than 8). PHEs thus are analysed easily using the computer recognition program.

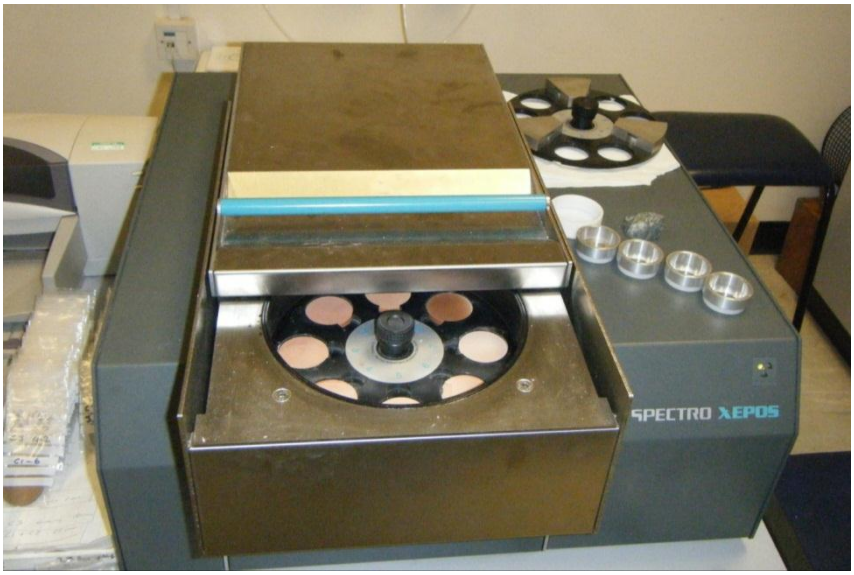


Plate 2: Spectro Xepos X-Ray Fluorescence Spectroscopy with 8-disc holder.

2.4.6 Results prior to characterisation.

The results from the XRF analysis showed that the elements concentrations decreased in the sediments and increased in the zeolites. Table 2 shows the results for the main 7 elements for setups i, ii and iii (Section 2.4.3), using 100% zeolites in the mats, 50:50 PFA/Clinoptilolite and 100% PFA. The concentration of the major PHEs under investigation decreased in the sediments, Zn (47%), Pb (42%), Ni (26%), Cr (23%), Cu (21%), Cd (9%) and As (8%). On the other hand, the concentration of these elements absorbed by the zeolites increased, Cu (263%), Zn (138%), As (47%), Ni (12%), Pb (9%), Cr (0.07%) and Cd (0%). The effectiveness of the zeolites thus followed the series Cu>Zn>As>Ni>Pb>Cr>Cd.

In the second trial using zeolite and PFA, the concentration of PHEs decreased in the sediments but at higher percentages, Cr (54%), Cd (46%), Zn (45%), Pb (45%), Ni (52%), Cu (43%) and As (53%). The concentration of the PHEs absorbed by the zeolite/PFA increased considerably for some PHEs, Cu (4182%), Cr (1033%), Zn (99%), Ni (1601%), Pb (22%) and Cd (0%). On the other hand, As concentration decreased by 99% in the zeolite/PFA mixture. The selectivity of this combination followed the selectivity series Cu>Ni>Cr>Zn>Pb>Cd. These results have not been documented before as PFAs and zeolites have not been used in combination in other research.

In the third trial experiment using PFA only, the concentrations of PHEs also decreased in the sediments, Cr (39%), Cd (43%), Zn (52%), Pb (53%), Ni (72%), Cu (28%) and As (53%). The increase in concentration of PHEs in the PFA reflected the results from the other trial experiments with an increase of 743% for Cr, Cu (1220%), Ni (1900%), Cd (79%) and Pb (20%). On the other hand, concentrations of As and Zn decreased by 26% and 15%, respectively. Selectivity series of PFA was Ni>Cu>Cr>Cd>Pb.

Table 2 shows the results for these experiments. The concentration of PHEs ‘lost’ from the sediments did not equate to the concentration of PHEs adsorbed by the zeolite or zeolite/PFA combination. Some PHEs had high (>1000 mg/kg) concentrations unaccounted for in the sediments and thus would not result in the remediation experiments to be as effective as possible.

Table 2: Preliminary results & mass balance difference in trial experiments using clinoptilolite, Clinoptilolite + PFA & PFA. Concentrations in mg/kg

EXPERIMENT 1: CLINOPTILOLITE								
	n=8	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Sediment Before	Mean	531.63	300.34	5234.25	17158.75	79.09	73.75	1413.63
	SD	45.73	33.72	164.28	150.42	15.09	16.55	24.79
Sediment After	Mean	409.67	221.48	4131.56	9056.75	72.65	67.21	806.14
	SD	172.73	94.01	1899.06	2659.44	31.77	37.16	242.81
Difference		121.96	78.86	1102.69	8102.00	6.44	6.54	607.49
Zeolite Before	Mean	32.90	6.58	5.87	36.86	12.34	0.00	56.86
	SD	0.00	1.46	1.56	1.64	2.04	0.00	2.33
Zeolite After	Mean	32.93	7.36	21.28	87.73	18.14	0.00	61.77
	SD	4.56	1.43	4.76	20.50	2.09	0.00	2.95
Difference		0.02	0.79	15.41	50.86	5.81	0.00	4.91
Mass Balance		**121.93**	**78.07**	**1087.27**	**8051.14**	**0.63**	**6.54**	**602.58**
EXPERIMENT 2: PFA: CLINOPTILOLITE								
	n=8	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Sediment Before	Mean	834.75	584.25	5458.63	16202.50	173.63	124.99	1385.63
	SD	117.83	88.63	799.06	2193.05	33.47	38.99	192.73
Sediment After	Mean	384.63	281.14	3125.88	8835.88	81.18	67.80	760.23
	SD	65.81	47.02	556.69	1406.06	13.74	12.59	122.60
Difference		450.13	303.11	2332.75	7366.63	92.45	57.19	625.40
Zeolite Before	Mean	40.23	5.68	6.32	35.23	17.30	0.00	53.86
	SD	1.21	2.40	2.48	6.31	4.41	0.00	9.52
Zeolite After	Mean	455.88	96.63	270.80	70.38	1.46	0.00	65.54
	SD	83.74	25.07	44.56	5.14	0.44	0.00	3.09
Difference		415.65	90.95	264.48	35.14	-15.84	0.00	11.69
Mass Balance		**34.48**	**212.17**	**2068.27**	**7331.48**	**108.29**	**57.19**	**613.71**
EXPERIMENT 3: PFA								
	n=8	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Sediment Before	Mean	711.75	457.38	10312.00	19352.50	119.13	108.53	1504.38
	SD	36.06	16.73	487.39	247.14	4.94	12.50	28.43
Sediment After	Mean	434.88	126.73	7387.38	9292.50	56.45	61.54	702.75
	SD	22.35	7.80	182.85	175.56	4.10	9.12	11.63
Difference		276.88	330.65	2924.63	10060.00	62.68	46.99	801.63
PFA Before	Mean	34.46	7.09	4.81	67.80	48.15	9.60	58.79
	SD	0.86	2.00	0.49	1.56	2.08	8.65	3.23
PFA After	Mean	290.78	141.75	63.53	57.93	35.46	17.12	70.85
	SD	10.15	34.02	6.31	10.18	4.75	84.79	22.59
Difference		256.32	134.66	58.71	-9.87	-12.69	7.52	12.06
Mass Balance		**20.56**	**195.99**	**2865.91**	**10069.87**	**75.37**	**39.47**	**789.57**

2.4.7 Discussion of remediation pilot study

As discussed in Section 2.3.1, zeolites have been used in previous research (Blanchard *et al.*, 1984; Ouki *et al.*, 1994; Inglezakis *et al.*, 2002; Inglezakis *et al.*, 2003; Inglezakis *et al.*, 2007; Stylianou *et al.*, 2007; Babel and Kurniawan, 2003; Feng *et al.*, 2000) and different zeolites have shown different selectivity series. Clinoptilolite has a high affinity for Pb but this was not observed in the trial experiments. The selectivity series in the trial experiments was Cu>Zn>As>Ni>Pb>Cr>Cd, as shown in Table 2. The selectivity series did not follow the same selectivity series observed by other researchers where the selectivity series was often Pb>Cu>Cd>Zn>Cr>Co>Ni (Inglezakis *et al.*, 2002; Stylianou *et al.*, 2007; Ouki *et al.*, 1994; Ouki and Kavannagh, 1997). Zn and Cu were the main PHEs absorbed by the zeolites. These two PHEs follow sorption mechanisms in parallel (Stylianou *et al.*, 2007) and Zn does not occupy the same sites on the zeolites as other divalent cations and therefore there is no competition for these sites (Badillo-Almaraz *et al.*, 2003; Inglezakis and Loizidou, 2007). A possible explanation for the change in the order of elements in the selectivity series could be a function of the complex and diverse compositional nature of canal sediments, as described by Wragg and Cave (2009a).

Since the samples for the trial experiments were homogenised and taken randomly within each tank, the apparently low efficiency of the zeolites to absorb the PHEs could be due to experimental error. The extent to which the zeolites absorbed PHEs was unknown and taking a mean value from the whole tank decreases the efficiency results. For example, the absorbent could have absorbed 100% PHEs from the zone close to the absorbent mat but nothing from the bottom of the tanks which would result in skewed results. A more detailed approach was needed and the sediments needed thorough characterisation within each tank through the depth profile of the tanks. The characterisation methodology (Chapter 4) describes the new approach with virtually three layers (not as a function of geological time record but as zones or sample points) and using a multi-proxy approach to understand processes occurring in the sediments from the top of the sediment pile to the bottom of the tank.

Pulverised fuel ash has mainly been used as the raw material for the synthesis of zeolites as discussed in Section 2.2.3. The aim of this research was to evaluate the effectiveness of the PFA to absorb PHEs and water and the results from the trial experiments showed that they were effective for most of the PHEs, except for As and Zn. PFA usually has a high pH which limits the leachability of PHEs (Sear and Weatherley, 2003). Zn is present at concentrations in

PFA which allows an economic recovery but is only leached at low pH values (Nagib and Inoue, 2000) which would have been highly unlikely in the canal sediments. The leaching of As from the PFA on the other hand suggests that they were present in their oxyanionic form (Jankowski *et al.*, 2006).

The main observation from all the trial experiments was the mass balance difference. There was a difference in the concentration of PHEs in the sediments after the experiments which did not match the increase in concentration of the same PHEs in the absorbent (clinoptilolite and/or PFA). The results suggested that the behaviour of the PHEs were dependent on secondary processes occurring in the sediments after they are dredged, for example, Redox potential, pH, bacteria and oxygen availability. A possible explanation for the difference in concentration in the sediments before and after the experiments could be due to the PHEs going into solution.

The main question that arises from the mass balance difference is- where are the PHEs? The XRF results defined a mean total concentration of the PHEs within each box and therefore the exact location of these PHEs was unknown. For example, it is unclear whether the elements have or have not been mobilised from the bottom of the boxes. The PHEs could be either in solid phase or liquid phase but the supernatant and pore water was not sampled before and after experiments to determine the pore water PHE concentrations. To determine the pore water concentration, a new method has to be implemented as discussed later in the thesis. Moreover, even with total concentration and pore water concentration, the main processes occurring within the sediments, such as Redox and pH can affect the efficiency of the zeolites. The effects can be positive or negative and thus more information is needed on the associations of PHEs in the sediments with other phases such as organics, oxides, sulphides/sulphates, or residual. The apparent discrepancy in the mass balance difference could possibly be due to the solubilisation of elements due to oxidation and/or biological processes.

The PHEs are taken up by the sorbents by processes such as adsorption and absorption. Clinoptilolite mainly adsorbs due to the functional groups present on the surface of clinoptilolite (Argun, 2008). The functional groups are silica (Si)–O (H)–Si, Si–O (H)–Al, Si–O–Si and Si–O–Al. The results from the XRF in this pilot study gave a good overview of the total concentrations of PHEs in the sediments but using XRF alone did not provide enough information on processes such as absorption/adsorption, mobilisation and/or solubilisation. Efficient remediation can only be achieved if these processes are understood both for the

sediments and zeolites; the secondary processes after dredging for the sediments and processes of sorption for the zeolites.

Other factors such as competition between cations, presence of organic matter and cation exchange capacity can also affect the efficiency of the zeolites (Babel and Kurniawan, 2003). The presence of Cr for example reduces the efficiency of clinoptilolite to adsorb Cd and Pb (Ouki and Kavannagh, 1997), possibly due to presence of ligands that form complexes with reduced accessibility and/or affinity for ion exchange (Vaca Mier *et al.*, 2001). The results from the trial experiments do not correspond to other research outcomes, where Pb and Cd were effectively adsorbed by clinoptilolite (Langella *et al.*, 2000; Sprynskyy *et al.*, 2006). This could be due to the compositional nature of the canal sediments, a multi-component system where competitive reactions decrease removal efficiency (Jha *et al.*, 2008). Organic matter can also affect the removal efficiency as increased organic matter would restrict availability of metals such as Cu or Cd (Elliott *et al.*, 1986). Cation exchange capacity is also strongly related to PHE cation adsorption and affects Cd, Cr, Ni and Pb (Gomes *et al.*, 2001).

One of the other aims of the remediation trial was to assess the effectiveness of zeolites and PFA to absorb water as well as PHEs which would stabilise these sediments and potentially change their status (their status being ‘liquid’ after they are dredged according to the Environment Agency). Both zeolites and PFA were effective in absorbing the supernatant which meant that both zeolites and PFA were effective for dewatering of canal sediments. On the other hand, the lack of water/supernatant is a disadvantage to determine if PHEs reside in the aqueous phase. The characterisation experiments (Chapter 4) were thus designed to provide ample aqueous sample for ICP and IC analysis.

The overall design for the remediation trial experiments were based on reducing waste. Although the zeolites would have to be disposed in hazardous landfills afterwards, the volume of zeolites is considerably less than the volume of untreated sediments and thus would save British Waterways a significant amount of money. The voile pillow cases were used so that they could easily be removed once the treatment was over and the zeolites/PFA could be either reused or disposed of. From the remediation pilot study, it can be deduced that the pillow case mats were an effective way to apply the zeolites as long as the PHEs are in solution and are in contact with the zeolites through the capillary action. The pore water moves against gravity and is absorbed by the zeolites which act like a sponge.

2.4.8 Conclusion

It was concluded from the results that more information was needed on the conceptual understanding of all remediation processes, especially concerning the mobility of elements within the canal sediments and those factors that contribute to their mobility. Moreover, the design of the remediation setup was dependent on the movement of the elements from the sediments to the zeolites through the voile mats which meant that the elements had to be mobile to do so. The mass balance difference was seen in all three experiments, the one with zeolites only, one with PFA only and the last setup with half zeolite and half PFA.

The results from the remediation trial experiments were ambiguous and thus the research was redesigned to focus on characterisation of the sediments first (as discussed from Chapter 3 onwards) to elucidate processes occurring after dredging. From preliminary results, it was also concluded that although the voile mats were effective to some extent, it was not good enough to achieve maximum efficiency of the zeolites/PFA to absorb PHEs in the sediments. The different combinations of zeolites and PFAs would still be used as the zeolites/PFA are effective for the whole range of PHEs, as discussed in Section 2.3.1.

CHARACTERISATION OF CANAL SEDIMENTS

CHAPTER 3

"In the confrontation between the stream and the rock, the stream always wins- not through strength but by perseverance."- H. Jackson Brown

CHAPTER 3

CHARACTERISATION OF CANAL SEDIMENTS

3.1 CANAL SEDIMENTS

Sediments are particulate matter that can be transported by fluid flow and which are eventually deposited as a layer on the bed or bottom of a body of water, in this case, canals. Canal sediments comprise minerals and organic solids, aqueous and gaseous components. The minerals are usually weathered rock sediments and secondary minerals, such as phyllo-silicates or clay minerals, oxides of iron, Al or Mn and sometimes carbonates (Alloway, 1990). Organic matter can comprise of dead plant materials and colloidal humus. Canal sediments are usually in an anoxic/anaerobic environment (Dodd *et al.*, 2003), which has an effect on other factors that affect processes occurring within the sediments. The sediment system is affected by changes in pH, Redox conditions and oxygen availability which, in turn, affect the mobility and availability of metals in the sediments. Canal sediments vary in particle size depending on the location and surrounding environment, ranging from very fine clay particles to silts and sands. Clay minerals often absorb the most PHEs, due to their large surface area and their permanent negative charge (Alloway, 1995). The octahedral cations between the clay layers are usually Al, magnesium (Mg) and iron (Fe), but can also in some cases be lithium, titanium, V, Cr, Co, Ni, Cu and Zn. Clay minerals rarely occur in pure form in soils and are usually attached to humic compounds or hydrous oxides. These oxides are usually of Fe, Al and Mn, which co-precipitate and absorb ions (positive when pH conditions are acidic and negative when conditions are alkaline) such as Co, Cr, Cu, Mn, molybdenum (Mo), Ni, V and Zn (Alloway, 1995).

3.2 THE AVAILABILITY OF POTENTIALLY HARMFUL ELEMENTS (PHEs) IN SEDIMENTS

The main concern for BW and local authorities disposing of canal sediments, is the potential contamination of local aquifers and surface waters after spreading. If the factors affecting solubility of the PHEs suddenly change, contaminants can be leached from the sediments into these water bodies and thus become bioavailable. Canal sediments can be very anoxic and at neutral to alkaline pH are unlikely to pose any risks as long as they are left undisturbed on the canal beds, as discussed with Proffitt and Beckwith (2008). Dredging on the other hand introduces rapid oxygenation of the sediments. Sulphides, for example, can oxidise and release

PHEs into solution. Canal sediments can be subjected to further pH changes in a landfill site by the action of slightly acidic rainfall, thereby releasing PHEs into the environment (Maes *et al.*, 2003).

3.3 TOTAL VERSUS AVAILABLE PHEs CONCENTRATION

Organisations responsible for setting up Soil Guideline Values (SGVs) do not specify a protocol for the determination of the total concentration of PHEs and thus make it difficult to use the SGVs as intervention values. Consequently, the errors between two or more analytical techniques which may be used to derive the same determinand lead to confusing and unreliable results. X-ray Fluorescence (XRF) spectroscopy has the advantage of being non-destructive, relatively simple and rapid to use (including sample preparation and analysis) compared to other methods, such as digestion and can be used for total concentrations of PHEs (Jones, 1982). Lithium metaborate (Licowax) is often used to fuse the sample at relatively low temperatures. The ratio of sediment to wax can often be high and thus dilute the elemental concentrations, sometimes below their detection limits (Ure, 1996).

Atomic spectrometric methods are also used for analysis of PHEs, which often requires complex digestion procedures involving various acids to dissolve the sedimentary matrix allowing for liquid analysis of the sample. The sediments are treated with acids and digestion of the sedimentary matrix is accelerated with the use of a microwave that enables higher pressure and temperature; essential for the dissolution of the sediments. Several researchers have used hydrofluoric acid (HF) to digest sediments and report that HF is the most effective acid for digesting the silicate matrix (Potts, 1992; Sandroni and Smith, 2002; Stephens *et al.*, 2001a; Sastre *et al.*, 2002). As canal sediments also contain a high percentage of organic matter, nitric acid is often used to break down the organic complexes. *Aqua Regia*, a mixture of nitric acid and hydrochloric acid, is a more effective acid for the digestion of sediments and soils to determine total concentration of PHEs (Sastre *et al.*, 2002; Stephens *et al.*, 2001a; Stephens *et al.*, 2001b). Hseu *et al*. (2002) postulated that the use of *Aqua Regia* revealed concentrations of PHEs closest to the true total concentrations. The US EPA have been using *Aqua Regia* since 1992, as their standard protocol (Method 1311, Toxicity Characteristic Leaching Procedure) for determination of PHEs in sediments (US EPA, 1992).

Although methods using *Aqua Regia* can give an accurate representation of the total concentration of PHEs in the sediments, the available concentration to the environment is

normally significantly lower. Cu for example can have a much higher total concentration in soils, but the information does not give any indication of its availability (Brun *et al.*, 1998). Remediation can be very costly depending on the size of the site and the type of contamination and thus authorities are now putting more emphasis on preliminary research to determine available rather than total concentrations of PHEs before proceeding with a remediation strategy (Brun *et al.*, 1998).

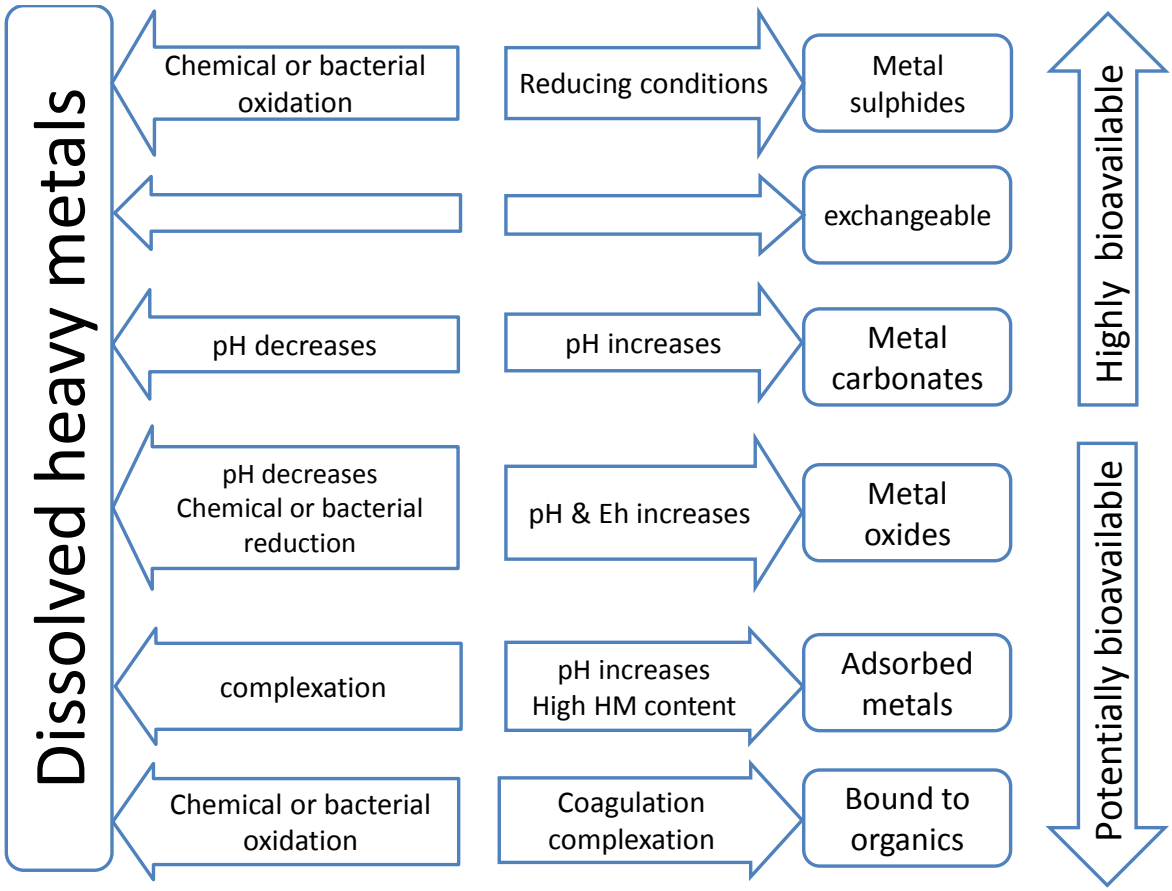


Figure 5: Factor affecting bioavailability of PHEs, after Demars *et al*. (1995).

In order to achieve this, all the factors affecting the behaviour of the PHEs in the sediments, as shown in Figure 5, have to be considered. The Environment Agency uses a leachate test to determine the availability of PHEs in sediments (Lewin *et al.*, 1994). Leaching is carried out by adding to the required sample weight, a volume of water left overnight to attain carbonate equilibrium (pH 5.6) to give a 10:1 ratio of water to soil. The bottle is tumbled at a rate of 0.5 revolutions per minute at room temperature for 24 hours. The resultant leachate can then be analysed for any parameters desired (Lewin *et al.*, 1994).

3.4 CHALLENGES FOR ASSESSING BIOAVAILABILITY

Since available concentrations are favoured to total concentrations, some researchers are assessing the bioavailability of PHEs using phyto-research (Ge *et al.*, 2002; Peijnenburg *et al.*, 2000; Brun *et al.*, 1998). The problem arises when different plant species absorb different amounts of metals (Brun *et al.*, 1998). Alternatively, researchers have also investigated the bioavailability of PHEs in humans, specifically in the human gut and gastro-intestinal tracts (Cave and Wragg, 1997; Ruby *et al.*, 1996). Other researchers, such as Brun *et al.* (1998) and Mellum *et al.* (1998), used various extractants such as diethylenetriaminepentaacetic acid (DTPA), ethylenediamintetracetic acid (EDTA), ammonium nitrate and calcium chloride to show the transfer of PHEs from soil to plants. Results showed good correlation of Cu with calcium chloride extractant and ammonium nitrate extractant, but similar to the human gut research (Cave and Wragg, 1997; Ruby *et al.*, 1996), provide only a good insight for plants and humans but not the general and potential contamination to the wider environment. Other researchers have also used deionised water as an extractant to assess the leachability of the sediments with regards to the pH conditions (Abollino *et al.*, 2002; Stephens *et al.*, 2001b; Lewin *et al.*, 1994). Varying the pH and Redox conditions under experimental conditions can be quite complex due to the buffering capacity of the sediment (Pagotto *et al.*, 2001; Xu *et al.*, 1991). The pH can be changed using nitric acid or NaOH (Kedziorek and Bourg, 1996), but experimental analysis would require the measurement of the pH to be taken individually and thus impractical in the case of batch experiments. Other researchers have used apparatus capable of controlling the pH of samples automatically and have more accurate readings (Maes *et al.*, 2003; Gäbler, 1997; Chuan *et al.*, 1996) but again would not be appropriate when analysing batch samples and would be too costly in such instances.

3.5 GEO-CHEMICAL CHARACTERISATION OF CANAL SEDIMENTS

Since canal sediments have varying pH and are anoxic, the PHEs are either precipitated or attached to the sediment or dissolved in the pore waters. According to Tessier *et al.* (1979), PHEs are associated with five fractions in sediments: exchangeable, carbonate bound, Fe and Mn oxide bound, organic fraction and residual fraction. The exchangeable fraction can be affected by changes in ionic composition of the water as well as sorption-desorption processes. The carbonate fraction can be affected by pH, whereas the Fe/Mn fraction can be thermodynamically unstable under anoxic conditions. The organic fraction on the other hand can release soluble metals under oxidising conditions with degradation of the organic

compounds. Finally, the residual fraction is the one not affected by changing conditions, although the mineral crystals that hold the PHEs can be altered over extended geological time periods (Zorpas *et al.*, 2008).

Canals have to be dredged and, as reported earlier (Section 1.1), dredgings cannot be sent to general landfill sites in some cases (Stephens *et al.*, 2001a). It is important to characterise canal sediments as they are mainly anthropogenic and markedly different from most natural sediments (Bromhead and Beckwith, 1994; Bijlsma *et al.*, 1996; Galvez-Cloutier and Dubé, 1998; Boyd *et al.*, 1999; Dodd *et al.*, 2000). Moreover, when these sediments are moved from the canal to the land, there is a potential change in Redox potential, normally to oxidising conditions, which can affect the associations and speciation of the potentially harmful elements (PHE) in the sediments (Cook and Parker, 2003). Oxidation may result in increase in the bioavailability of these elements (Caplat *et al.*, 2005). Tack and Verloo (1995), Singh *et al.* (2006) and Stephens *et al*., (2001a) have all illustrated the need for further characterisation.

In the UK, Kelly *et al.* (1996), Dodd *et al.* (2003) and Large *et al.* (2001) have researched the characterisation of canal sediments. Kelly *et al.* (1996), compared Wolverhampton, an established industrial area, and Richmond-upon-Thames, a non-industrial area, to show the distribution of Zn correlating with both high traffic density and past industrial activity. Heavy metal provenancing (Appasamy, 2006) further supports the evidence that PHEs stay in sediments for a long time, as particular PHE concentrations in canal sediments strongly correlate to relict industries on archive maps showing past industrial activity. The areas of East and South East Wolverhampton are well-known for past industrial activity in Fe-related industries, engineering works and metal workings (Kelly *et al.*, 1996). Research on canal sediments in the West Midlands have been conducted before, but are often focused on specific PHEs. Dodd *et al.* (2003), for example, focused on the geochemistry and petrography of phosphorus in urban canal sediments. Dodd *et al.* (2003) asserted that the most common minerals found in sediments are sulphide minerals, which are often major sinks for PHEs. Sulphide minerals include Fe, Cu and Zn sulphides and are of major interest when studying characterisation of canal sediments (Large *et al.*, 2001).

Since Europe has an extensive network of canals, researchers in other European countries such as France, Germany and The Netherlands have also studied canal sediments. Research is even more important in these countries as an increasing amount of freight is being transported along

navigable waterways that need regular dredging. Capilla *et al*. (2006) reported on the effects of PHEs in the dredged sediments of the River Rhine and their effects on plants, and concluded that PHEs in the sediments were mostly associated with two phases, iron oxides and alumino-silicates. The iron oxides and alumino-silicates accumulated in the aerial parts of the plants, but the main research aim was to derive a classification for these sediments. Although Capilla *et al.* (2006) studied Cd, Pb, Fe, Cr, Zn, and Cu in canal sediments, other PHEs such as As, Se, Sr, Ni and Hg, and secondary processes in the sediments were not studied and thus the research did not present a full overview of the state of the sediments. Similar studies have been conducted in Spain and Turkey, where dredging-disposal problems similar to the UK have been found (Coz *et al.*, 2007; Akcay *et al.*, 2003; Casado-Martínez *et al.*, 2007). Although the majority of research conducted on sediments considered the elemental concentration of PHEs, only Coz *et al.* (2007) considered the speciation of these metals. Conventionally, the total metal content of canal sediments is determined, giving an approximate approach to understanding the role of metals as pollutants, but in most cases PHE bioavailability is not considered (Perin *et al.*, 1997b; Chojnacka *et al.*, 2005). A higher total concentration of PHE does not necessarily imply higher toxicity. For example, Cr is very toxic as Cr(VI) but is an essential element as Cr(III) (Fuentes *et al.*, 2004a; Akcay *et al.*, 2003). Sediments in estuaries, river and lagoons in many cases exhibit anoxic conditions similar to canal environments and present the same conditions linked to metal binding by the sulphides, Mn oxides and Fe oxides (Perin *et al.*, 1997a).

3.6 SEQUENTIAL EXTRACTION

Determining the total concentration of PHEs in contaminated sediments is insufficient to assess the behaviour of contaminated soils and thus sequential extraction was developed in the 1970s to determine the concentration of the PHEs in each fraction (Chen *et al.*, 2007). Since Tessier's sequential extraction procedure in 1979, several researchers have developed improved versions of this procedure with extra fractions being considered with the five fractions mentioned in Section 3.5. Amongst the most popular methods was the Kersten and Forstner (1986) method which was developed from Tessier's especially for anaerobic sediments (Usero *et al.*, 1998). Then, the European Bureau Communautaire de Reference (BCR) developed a new sequential extraction method to harmonise the numerous existing sequential extraction procedures (Dodd *et al.*, 2000; Adamo *et al.*, 2003). This method has been successfully used to determine concentration of PHEs in the different fractions for lake, lagoon and marine sediments, sewage

sludge, soils and industrially contaminated sediments (Fuentes *et al.*, 2004b; Fuentes *et al.*, 2004a). The Kersten and Forstner (1986) method involves a four stage procedure whereas the BCR had only three stages. Many researchers now use the BCR method as reference with minor changes to accommodate the smaller fractions that they are considering in their research (Caplat *et al.*, 2005; Fuentes *et al.*, 2004a; Fuentes *et al.*, 2004b; Guevara-Riba *et al.*, 2004).

Remediation cannot be maximised if characterisation of the polluted sediment has not been considered. Since the PHEs have such 'random' behaviour with different conditions and varying parameters, remediation will not be effective if the exact form and location of the PHEs in the sediments are unknown, especially when several pollutants are being considered at the same time (Oman and Junestedt, 2008).

The results of the sequential extraction procedure often give a better understanding of the pollution level and type of contaminant. The surplus concentration of PHEs usually introduced by external sources is often in unstable chemical forms. Moreover, a relatively low concentration of PHEs in the exchangeable fraction shows that the sediments are relatively unpolluted (Abd El-Azim and El-Moselhy, 2005). Sequential extraction procedures are useful to distinguish between anthropogenic and geochemical sources of PHEs in sediments. Concentrations of PHEs in Fraction 1 to 4 (Tessier's), as shown in Table 3, are very important as PHEs associated with these fractions can be released in the environment if there are changes in pH, Redox potential or in the presence of natural or synthetic chelators, as outlined by Abd El-Azim and El-Moselhy (2005).

Table 3: PHEs associations with the different fractions in canal sediments (Tessier's Fractions) (Tessier *et al.*, 1979)

Stages	Fractions
1	Exchangeable
2	Carbonate
3	Iron/Manganese Oxide
4	Organic
5	Residual

These conventional methods have their limitations. During the extraction, there is often re-sorption of cations and redistribution among different phases (Förstner, 1993; Tack and Verloo, 1995; Robertson *et al.*, 2003). Although this is not a substantial amount, it is still an important factor to consider as this can compromise the interpretation of the results. In

addition, the choice of reagents is also crucial. Reagents used for the highly exchangeable fractions should be wisely considered. Nitrates are usually preferred as there is no selectivity problems compared to acetates and chlorides, which allow transfer in solution of metals that are not necessarily bound to these active sites (phyllosilicates and phyllomanganates). The pH is also vital, for example when dissolving the carbonates fraction with a mixture of sodium acetate and acetic acid, the pH used is usually 5. It has been shown by research that sodium acetate solution at pH 5 is not efficient in dissolving carbonates and that it should be lowered to 4.5 (Leleyter *et al.*, 1999). Sodium dithionite is often used for the extraction of the Fe and Mn phases, but this reagent attacks clay minerals. Instead, hydroxylammonium is preferred to reduce Mn, but here again this is not suitable for Fe oxides (in low temperatures and low concentrations). A more recent but more effective sequential extraction procedure was developed by the British Geological Survey (BGS) - the Chemometric Identification of Substrates and Element Distribution (CISED) extraction method (Cave *et al.*, 2004). It uses a single extractant at varying concentrations and following the seven stages of extraction, the data are subjected to a multivariate analysis to determine the associations. The sequential extraction procedure has many advantages over its predecessors. The following describes the disadvantages of the previous methods that have been rectified with the CISED method, as illustrated by Cave *et al.* (2004).

a) The extracting reagents are difficult to analyse and are not specific for particular mineral phases.
b) The methods are time consuming and complex to carry out and inappropriate for large sample batches.
c) The reaction times are long and often lead to elements to be reabsorbed from a target phase to other phases giving flawed results.
d) There is no standardised method and thus no comparison between different data as different users modified established methods to suit their own demands in terms of particular soils or elements being sought.

3.7 POTENTIALLY HARMFUL ELEMENTS (PHEs)

The term heavy metals was originally intended to describe those metals with an atomic density greater than that of Fe, but is now understood to encompass elements with an atomic density > 6 g/cm^3 or an element with an atomic number >20 (Forstner and Calmano, 1998; Alloway, 1990). However, because As is also considered as a heavy metal, although being a metalloid,

the term trace elements are now widely used to avoid confusion. Metals/metalloids can be grouped according to their behaviour in the environment. Table 4 shows the heavy metals under study in this research and their properties. Although it is not a quantitative scheme, it is useful in grouping elements according to their behaviour. The mobility of these elements in the environment is often illustrated using the soil-plant transfer coefficient (Kloke *et al.*, 1984). The coefficient is affected by pH, soil organic matter and plant genotype and based upon root uptake. The transfer coefficients in Table 4 illustrate the high mobility of Cd and Zn in the soil-plant system but the lower mobility of Cr, Pb, As and Cu. However, for the purpose of this research, the term potentially harmful elements (PHE) will be used, as it is the accepted term used by the International Union of Pure and Applied Chemistry (IUPAC), the world authority on chemical nomenclature, terminology and standardized methods for measurement (Duffus, 2002). Ni, Cu and Zn are included in the list of PHEs due to their phytotoxicity.

Table 4: PHEs characteristics

Element	Oxidation states	Ionic radius (nm)*	Geochemical classification **	transfer coefficient***
Cd	**2**	0.097	chalcophilic	1.00-10.00
Cr	**2,3,6**	0.069 (+3) 0.052 (+2)	lithophilic	0.01-0.10
Cu	**1,2**	0.096 (+1) 0.069 (+2)	chalcophilic	0.01-0.10
Zn	**2**	0.074	chalcophilic	1.0-10.00
As	**3,5**	0.222 (-3) 0.047 (+5)	chalcophilic	0.01- 0.10
Pb	**2,4**	0.120 (+2) 0.084 (+4)	chalcophilic	0.01-0.10
Ni	**2,3**	0.078 (+2) 0.062 (+3)	siderophilic	0.10-1.00
* Stark & Wallace (1982), ** Krauskopf & Brid (1995), *** Kloke *et al.* (1984).				

3.7.1 Cadmium (Cd)

Cadmium is a highly toxic metal and in humans accumulates in the kidneys and can cause dysfunction if concentrations exceed 200 mg/kg (fresh weight) (Di Toro *et al.*, 1990). Cd in soils originates mainly from industrial sources, such as smelting and mining. In soil solutions, it is mainly present as Cd^{2+} free ions or as complex ions such as chlorides and hydroxides and as organic complexes. Cd is more mobile than other PHEs in soils due to the lower affinity of

some soil constituents for this metal (Aboulroos *et al.*, 2006). The specific adsorption of Cd is controlled primarily by pH, organic matter and hydrous oxide contents of soils. Cd adsorption can be inhibited by competitive ions, such as Ca, Co, Cr, Cu, Ni and Pb. In canal sediments where the conditions are highly anoxic, Cd forms CdS, which is less bioavailable than oxidised forms of Cd. Cd is also strongly associated with Zn, although Cd exhibits higher mobility than Zn when acidic conditions prevail. Cd also has a stronger affinity for sulphur than Zn. Adsorption to mineral surfaces in soils controls Cd concentration rather than precipitation (Farrah and Pickering, 1977; Tiller *et al.*, 1979). Solubility of cadmium carbonate ($CdCO_3$) and possibly cadmium phosphate ($Cd_3(PO_4)_2$) control solubility of Cd, so Cd is not easily mobile above pH 7.5 (Tiller *et al.*, 1979). The amount of Cd in sediments is closely related to acid-volatile sulphides (Di Toro *et al.*, 1990; Bryan and Langston, 1992).

3.7.2 Copper (Cu)

Cu is one of the least mobile PHEs in soils as it is fixed or specifically adsorbed by organic matter. Owing to this affinity for organic matter, the total Cu concentration in surface soils is usually only 0.01 to 0.6 µM (Baker and Senft, 1995). The COO- group, which is prevalent in organic matter, forms stable complexes with Cu. Cu^{+} is more stable under reducing conditions whereas Cu^{2+}, the most common form of Cu is more frequent under oxidising conditions. The Cu^{2+} in soils can be chemisorbed onto, or occluded in, Fe and Al oxides and silicate clays and also occluded as carbonates. In oxidised surface sediments, Cu is associated with Fe-Mn oxides and organic components such as humics (Luoma and Bryan, 1981). Cu is one of the elements that is less mobile, being specifically adsorbed or ‘fixed’ in soils (Alloway, 1995).

3.7.3 Lead (Pb)

Pb occurs mainly as galena (PbS) due to its highly chalcophilic properties. During weathering, Pb sulphides slowly oxidise and Pb^{2+} ions can form carbonates and be incorporated in clay minerals, Fe-Mn oxides and organic matter (Hatje *et al.*, 2003; Singh *et al.*, 2006). Pb can cause toxicity in adults and neurological impairment in children. Due to the low solubility of Pb, it can accumulate in sediments and remain bioavailable for many years as it is also relatively free from microbial degradation (Davies, 1995). Lead in the environment comes mainly from mining and smelting, parent material, sewage sludge and historically from compounds in leaded petrol. Pb is mainly present in soils in the soil humus, silicate lattices, as precipitated forms, secondary Mn and Fe oxides, alkaline earth carbonates and on the

adsorption surfaces of the clay-humus exchange complex. Pb in sediments alters with Redox, changing from oxy-compounds to PbS if anoxic conditions prevail (Fergusson, 1990).

3.7.4 Arsenic (As)

As forms part of the metalloid group, although it forms anionic species and is not technically considered a heavy metal (Genc-Fuhrman *et al.*, 2007; Fergusson, 1990). The stable states of As are As^{3+} and As^{5+}. As^{5+} is less soluble and less toxic than As^{3+}. Arsenic sources in the environment, include smelting of metal ores, burning of coal, tanning and textiles industries and the electronic industry. As is toxic to living organisms and is thus a major concern for authorities dealing with waste containing the metal. As minerals and compounds are readily soluble but mobility is greatly reduced by strong sorption to clays, hydroxides and organic matter (Kabata-Pendias and Pendias, 1984). As concentration in sediment pore water is affected by adsorption onto oxide phases, solid phase As concentrations and Redox conditions. As^{3+} (arsenite) to As^{5+} (arsenate) conversions are particularly sensitive to Redox changes and so although arsenate is thermodynamically favoured in surface waters, arsenite (more toxic) may prevail in anoxic pore waters (Peterson and Carpenter, 1986). As dissolved at depths diffuses upwards and is often adsorbed onto precipitating Fe-Mn oxides (Bryan and Langston, 1992).

3.7.5 Chromium (Cr)

Cr is a transition metal with Cr^{3+} and Cr^{6+} oxidation states being the most stable in sediments (Stephens, 2001), where Cr^{6+} is the most toxic and mobile species. Cr(III) is found predominantly in relatively unpolluted soils and is an essential element for humans, whereas Cr(VI) is mainly the result of anthropogenic activity. Cr(III) is an essential element, whereas Cr(VI) is toxic, carcinogenic and mutagenic. Sources include leather tanning, paints, preservative in wood and textiles, video audio tapes and additives to steel alloys. Under oxidation condition the chromate ions (CrO_4^{2-}), which are readily mobile and easily sorbed by clays and hydrous oxides (Kabata-Pendias and Pendias, 1984), forms the Cr^{3+} ions which are only mobilised in very acidic conditions. Cr^{6+} is easily mobilised in acid and alkaline soils.

3.7.6 Zinc (Zn)

Zn occurs in the Earth's crust mainly as zinc sulphides (ZnS), but is also known to substitute Mg^{2+} in silicates. Zn minerals are solubilised during weathering resulting in mobile Zn^{2+}, especially in oxidising environments (Kabata-Pendias and Pendias, 1984). Zn is easily and strongly adsorbed by clay minerals and organic components (Lindsay, 1972). Zn is readily

soluble relative to other PHEs, in soils and is the most mobile and readily available in acid light mineral soils. Zn associated with Fe-Mn oxides is the most available phase to plants (Norrish, 1975).

3.7.7 Nickel (Ni)

Ni is prevalent in its solid phase in soils as nickel ferrite ($NiFe_2O_4$) (Sadiq and Enfield, 1984). In acidic and reducing conditions, Ni sulphides are most likely to control Ni concentrations in soil solution. During weathering, Ni is mobilised and subsequently co-precipitated with Fe-Mn oxides (Kabata-Pendias and Pendias, 1984). This fraction is also the most available to plants (Norrish, 1975). Ni distribution is mostly affected by organic matter or amorphous oxides and clays depending on soil types (Kabata-Pendias and Pendias, 1984). Mobility is increased with a change in Cation Exchange Capacity (CEC) and hence an increase in plant uptake.

3.8 POTENTIALLY HARMFUL ELEMENTS AND CANAL SEDIMENTS

Internationally, the City of Delfe in The Netherlands is one of the pioneer sites in the study of canals and PHEs or other pollutants in canal sediments (Kelderman *et al.*, 1998; Kelderman *et al.*, 2000; Qu and Kelderman, 2001). More emphasis is now put on the disposal of canal sediments when they are dredged, especially with new and constantly changing European regulations (Section 1.4) regarding waste disposal (Donze, 1990). The Delfe canal system in the inner city is about 6.5 km long with an open water area of 55,000 m^2 (Kelderman *et al.*, 2000). It is connected to the Rhine by the Rijn-Schie canal and is the main shipping route for the Delfe-Rhine area. The pollutants in the area were exceeding Dutch quality standards and a thorough study was thus conducted over a larger area, including outskirts of the Delfe inner city over a period of 5 years (from 1991-1996) (Kelderman *et al.*, 1998; Kelderman *et al.*, 2000; Qu and Kelderman, 2001). Fifty one sample sites were chosen and tested for PHEs and other pollutants. The PHEs tested were Cd, Cr, Cu, Ni, Pb and Zn using Atomic Absorption Spectrometry (AAS). Seventeen out of the eighteen samples in the inner city were considered as moderately to highly polluted, which was considered as unacceptable by the Dutch regulations (Kelderman *et al.*, 2000). It was also found that the Rijn-Schie canal is the main contributor of PHEs in the inner city canal system. Overall, the results of this study show a decrease in Pb over the past decade due to new regulations in the European Union, concerning lead-free petrol, for example. Kelderman *et al.* (1998; 2000; 2003; 2007), also contributed to other studies in that area especially related to provenancing, as it was suggested by previous research that the River Rhine is a contributor of PHEs in the inner canal sediments in Delfe.

Canals and waterways sediments have also been widely studied in France and Europe in general, where characterisation of sediments and their roles as pollutant sinks along with potential remediation strategies were researched (Bianchini *et al.*, 2002; Adamo *et al.*, 2003; Capilla *et al.*, 2006; Vdovic *et al.*, 2006; Argese *et al.*, 1997; Caplat *et al.*, 2005; Boughriet *et al.*, 2007; Guevara-Riba *et al.*, 2004; 2005; Vandecasteele *et al.*, 2003). In the UK, several researchers have also studied characterisation and remediation of canal sediments but often tend to focus on a limited number of PHEs (Taylor *et al.*, 2003; Stephens *et al.*, 2001a; 2001b; Duquesne *et al.*, 2006).

3.9 SOURCES OF POTENTIALLY HARMFUL ELEMENTS

3.9.1 Geochemical sources- geology of the West Midlands area

Major and minor elements are found in the canal sediments. Major elements constitute over 99% of the element content of the Earth's crust (Alloway, 1995). The minor elements thus constitute < 1% of the Earth's elemental concentration. Canal sediments reflect this distribution with a higher proportion of major elements, such as O, Si, Al, Fe, Ca, Na, K, Mg, Ti and P compared with minor elements. Minor elements include Ag, As, Cd, Cu, Pb, Mo, V and Zn among others. Minor elements mostly occur as ores with other major elements, for example, Cr in chromite ($FeCr_2O_4$). Most ore minerals contain one or more minor elements. The bedrock and geology of the sampling area include a variety of sedimentary rocks ranging from sandstone to Coal Measures (Powell *et al.*, 1992). The sandstone is from the Clent Formation of the Permian. The Coal Measures are from the Carboniferous. Till or Boulder Clay is also found in this region originating from the Quaternary (Powell *et al.*, 1992).

3.9.1.1 Coal Measures

The Coal Measures were formed by cyclic subsidence and sedimentation due to changes in eustatic (sea-level fluctuations) status. The cycle "begins with marine or brackish shales which pass up through lacustine and deltaic deposits consisting of mudstones, siltstones and sandstone" (Powell *et al.*, 1992). Then colonisation of plants takes over, forming thick peats during periods of low subsidence. Finally, burial and compaction from subsequent cycles converted the peat into coal. The Coal Measures range in thickness from 94-152 m (British Geological Survey, 2008). Coal Measures consist mostly of mudstones and siltstones, fireclay and sandstone and coal seams, the latter comprising only 13-17% of the total thickness of the whole sequence.

3.9.1.2 Clent Formation

The Clent Formation consists of coarse-grained breccias set in a soft red-mauve mudstone matrix (Powell *et al.*, 1992). The pebble clasts consist of fragments from volcanic igneous rocks from the Precambrian rocks. In other areas, the breccia proportion decreases to give place to mudstones and thin beds of sandstone. The Clent Formation ranges from a thickness of 137-243 m (British Geological Survey, 2008).

3.9.1.3 Superficial (drift) deposits

The area from Wolverhampton up to Coseley was mostly on the margins of several glacial phases. Boulder Clay consists of brown or orange stiff clay mixed with other rock types originating from other areas (since they may have been eroded and transported by glaciers). Generally, the till deposits are thin ranging from 10-35 m (British Geological Survey, 2008).

3.9.2 Anthropogenic sources

There are several anthropogenic sources of PHEs. Since most of the PHEs are constituents of major ores, they become a by-product when the major elements are extracted from their ores. Mining and smelting are one of the main contributors of PHEs to canal sediments as they were the main activities associated with the Birmingham Canal Navigations area (Table 5 and 6).

Table 5: Key contaminants in industry around the Birmingham Canal Navigations (Environment Agency and Chartered Institute of Environmental Health, 2008)

		Key contaminants								
Industry		**As**	**Cd**	**Cr**	**Cu**	**Pb**	**Ni**	**Zn**	**S**	**PAH**
Charcoal works		√	√	√	√	√		√		
Chemical works		√	√	√	√	√	√	√	√	√
Engineering works		√	√	√	√	√	√	√	√	√
Gas works		√	√	√	√	√	√	√	√	√
Timber manufacturing works		√	√		√	√		√		√
Metal manufacturing refining & finishing:	Iron works	√		√		√	√	√	√	√
	Lead works	√	√	√	√	√		√	√	√
	Non-ferrous		√	√	√	√	√		√	√

Table 6: Industries along the BCN in 1888 (Appasamy, 2006)

Industries along the canal in 1888 (BCN)		
Bilston Gas Works	Galen Chemical Works	Victoria Iron Works
Shrubbery Works (iron)	Millfields Boat & Wagon Works	Chemical Works
Brick Works	Millfields Furnaces	Iron Tube Works
Bridge Foundry	Bilston Iron Works	Old Kilns
Tank and Boiler Works	Manor Iron And Tin Sheet Works	Bilston Road Bricks Works
Crown Nail works	Lanesfield Colliery	Ettingshall Iron Foundry
Wallsall St. saw mills	Spring Vale Furnaces	Mars Iron Works
Tank works	Staffordshire & Ingot Iron Works	Britannia Boiler tube works
Monmore Green Works	Springvale Foundry	Highfield boiler works
Atlas Works	Ladymoor Colliery	Minerva Iron & Steel Works
Cooperage Works	Springvale Colliery	Millfields Iron & Steel Works
Eagle Works	Ettinghsall Colliery	Breen Rhydding Colliery
Monmore iron works	Priorsfield Foundry	Boat Building Yard
Imperial Tube Works	Cannon Foundry (Hollow Ware)	Cement Works
Iron Works	Priorsfield Colliery	Deepfields Works-Sheet Iron
Deepfields Colliery	Deepfields And Coseley Station	Coseley Foundry
Hopyard Colliery	Hopyard Foundry Iron	Fullwoods End Colliery

Agricultural products also contain impurities (PHEs) which also end up in canal sediments. Some fertilisers and pesticides, for example, contain Cd, Cr, Mo, Pb, V and Zn, Cu, Hg and As (Alloway, 1995). Another contributor of PHEs in canal sediments is the metallurgic industries. Processes involved in the manufacturing of steel and alloys produce a whole range of PHEs which finally end up in the canal sediments through effluents or deposits. PHEs are also the by-products of many smaller industries, such as pharmaceutical, chemical and paint, printing and ink manufacturing, where they are also used as catalysts or stabilisers in many chemical processes (Dimirkou, 2007; Metes *et al.*, 2004; Chen *et al.*, 2003).

Fossil fuel combustion is also a source of a wide range of PHEs which end up in the canal sediments, for example, as airborne particles. Pb free petrol has been used during the last 20 years (Stephens, 2001) all over Europe, but historically petrol contained additives containing Pb. The other PHEs are deposited in the petrol and remain there until they are burnt. Other minor anthropogenic activities include military training and sports such as fishing, or hunting, with trace metal concentrations, especially Pb, in the bullets used (Alloway, 1995).

3.10 PROCESSES OF ABSORPTION

3.10.1 Oxidation Reduction

Oxidation and reduction also affect the amount of PHEs absorbed by the sediments. Redox (oxidation-reduction) status affects various elements for example carbon, nitrogen, oxygen, sulphur, Fe, Mn, Ag, As, Cr, Cu, Hg and Pb (Kelderman and Osman, 2007). Redox reactions in soils are usually catalysed by micro-organisms and depend on the availability of oxygen (Kelderman and Osman, 2007). Waterlogging and compaction in canals sediments reduces elements such as Mn, Cr, Hg, Fe, Cu and Mo (Förstner and Calmano, 1998). When Fe is reduced, for example, there is a slight pH increase in acidic soils and decrease in alkaline soils. In brief, reduction causes elements to be released in the soil solution when the hydrous compounds are dissolved by reduction (Stephens *et al.*, 2001b).

3.10.2 Metal oxides

With higher pH, the oxides of Fe precipitate before those of Mn. Small changes in pH can either give rise to dissolution or precipitation of Fe oxides. Reduction of Fe and Mn oxides use up the H^+ and therefore increase the pH of the soil, whereas oxidation lowers the pH. Mn provides space for surplus electrons to be stored. The colloidal Mn oxides have surface properties that are efficient for adsorption of inorganic and organic substances, whether cationic or anionic. These oxides act as scavengers for PHEs in soils and in waters by adsorption, complexation and Redox mechanisms (Sparks, 1999). Metal oxides and hydrous oxides of Al, Fe and Mn are important sorbents of PHEs (Redman *et al.*, 2002; Turner *et al.*, 2004; Sharma *et al.*, 2000). Fe and Mn oxides have lower crystalinity and higher adsorption capacity and thus are important, especially when considering PHEs (Turner *et al.*, 2004). The most common oxides in sediments are Fe oxides which range from a concentration of less than 0.1% to more than 50% in a uniform or sporadic distribution with crystals ranging from 5-150 nm (Turner *et al.*, 2004).

Fe can be released from Fe (III) oxides through protonation, reduction and complexation to produce Fe (II) cations and Fe complexes, respectively (Schwertmann, 1991). Deprotonation of the surface hydroxyl groups is favoured at pH 3-6 which results in higher trace metals sorption (Houben, 2004). Fe oxides have low solubility and the solubility of Fe from Fe oxides at pH 3-7.5 shows an inverse relationship (Byrne and Luo, 2000). Surface complexation is the main factor affecting sorption of metals onto the Fe oxides and under acid conditions the PHEs

are desorbed from these surface complexes as a result of proton exchanges. pH also controls the behaviour of these oxides as desorption of PHEs can increase with lower pH as the Fe oxides themselves start to dissolve. Different PHEs also behave differently, for example, lead is bound more strongly to Fe oxides than Cd. Finally, the crystallinity of the Fe oxide can affect the sorption capacity, as crystalline oxides have less functional groups and thus have lower sorption capacity (Houben, 2004).

Redox, like pH, has a major role in sorption or desorption of PHEs. Under reducing conditions, there is an increase in the dissolution of Fe and Mn (Chuan *et al.*, 1996; Tessier *et al.*, 1996) producing more mobile and soluble Fe (II) (Schwertmann, 1991; Schwertmann and Taylor, 1989). PHEs associated with Fe and Mn oxides are consequently released into solution. On the other hand, oxidising conditions are followed by precipitation of Fe oxides (Turner *et al.*, 2004). PHEs in other phases can become incorporated into the structure (Turner *et al.*, 2004). At lower pH, the organic coatings on the metal oxides increase the binding of PHEs (Tessier *et al.*, 1996). Moreover, lower pH increases precipitation of humic acids and fulvic acids onto the mineral surfaces (Simeoni *et al.*, 2003). Although more emphasis is put on Fe oxides, oxides of Mn are important. Fe oxides do absorb more PHEs (Turner *et al.*, 2004) and are often associated with Mn oxides in studies (Gélinas *et al.*, 1998; Tessier *et al.*, 1996; Voigt *et al.*, 1996), but Mn oxides have their role to play in metal binding, as illustrated by Hudson-Edward (2000) and McKenzie (1989). Al oxides occur in lower concentrations (Hsu, 1979) and are mostly studied together with the other oxides (Matera and Le Hecho, 2001; Xu *et al.*, 2001). Al oxides are important particularly when considering sorption of Pb (Zhuang and Yu, 2002), following surface complexation reactions (Bargar *et al.*, 1997). Al oxides can also bind other trace metals and this is enhanced by the sorption of organic matter to its surfaces (Shen, 1999; Tessier *et al.*, 1996).

3.10.3 Clay minerals & clay particle size fraction

Clay minerals play a major role in the partitioning of PHEs (Alloway, 1995). PHEs are bound to clays by surface binding, either by cation exchange or specific adsorption. Cation exchange is more prevalent at lower pH, whilst specific adsorption is more prevalent at higher pH (Weng *et al.*, 2001). Sorption can also occur in clay minerals such as micas and smectites with a 2:1 structure (Dubbin, 2000). Clay minerals also provide a site for organic matter and metal oxides to precipitate on. Organic matter increases the negative charge of the clay, while Al and Fe oxides have the opposite effect on surface charge (Zhuang and Yu, 2002). Clays are considered

both as a type of silicate minerals and also the percentage of the particles with a diameter of less than 2 µm (Rowell, 1994). Although this fraction contains mainly clay minerals, they can also be made up of fine ground particles of other minerals, such as Fe oxides, calcium carbonate, silicon dioxide and humic substances (Förstner *et al.*, 2001). The larger surface area of smaller particles makes particle size the most important factor for adsorption of PHEs (Droppo and Jaskot, 1995). The silt fraction together with the clay fraction makes up the fines (Cheshire *et al.* 2000). Christensen (1998) confirmed that PHEs are associated with organic matter as well as silts and clays.

3.11 MECHANISMS OF ABSORPTION

Absorption of PHEs occurs in sediments by the action of different mechanisms, although it is difficult to determine the precise mechanism in some soils. Absorption mechanisms are cation exchange, specific absorption, co-precipitation and organic complexation.

3.11.1 Cation exchange

PHEs exist mostly as cations in soil solutions, except for metalloids. Adsorption of metalloids depends on the density of negative charges on the surface of the soil colloids. To maintain electroneutrality, the negative charge is balanced by an equal quantity of cations which are then replaced by other cations with higher valency or with a higher degree of hydration. The higher the valency of the cation, the greater its replacing power (Fitzpatrick, 1986). Cation exchange can also be considered as the formation of outer-sphere complexes with the surface functional groups to which they are bound electrostatically (Alloway, 1990). The negative charges can be permanent and thus independent of pH due to the isomorphous substitution, or pH-dependent which occurs on the edge of clay minerals, polymers and oxides. The negative charges here are due to the dissociation of protons from carboxyl and phenolic groups on humic polymers and hydroxyls (OH groups) on the edge of clay minerals and oxides (Alloway, 1990).

3.11.2 Specific absorption

Specific absorption is dependent on pH changes and involves the exchange of the cations and anions of PHEs cations to form partly covalent bonds with lattice ions (Alloway, 1995). The difference is that specific absorption absorbs far more metal ions than cation exchange. Hydrous oxides of Al, Fe and Mn are thought to be the major constituents of soil that are involved in specific absorption. In addition to being absorbed on the surface of minerals, PHE ions also diffuse into minerals, such as goethite, illites, smectites and some other minerals. This

diffusion increases with pH up to a limiting point where it starts to decrease again (Ellis and Mellor, 1995).

3.11.3 Co-precipitation

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanisms and at any rate (Alloway, 1995). Clay minerals, hydrous Fe and Mn oxides and calcite, in which isomorphous substitution has occurred, are often formed. Other metals precipitate as solid compounds under physico-chemical conditions. Some of the PHEs that can precipitate as solid compounds are Cd, Cu, Pb, Mn, Hg, Mo and Zn. Table 7 shows the minerals and the coprecipitated trace elements.

Table 7: Minerals and coprecipitated elements (Alloway, 1995)

Mineral	Co-precipitated trace metals
Iron oxides	V, Mn, Ni, Cu, Zn, Mo
Manganese oxides	Fe, Co, Ni, Zn, Pb
Calcium carbonates	V, Mn, Fe, Co, Cd
Clay minerals	V, Ni, Co, Cr, Zn, Cu, Pb, Mn, Fe

3.11.4 Organic complexation

Another important factor to consider in the case of anoxic sediments is the organic complexation of PHEs. Humic acids absorb PHEs to form chelate complexes. Humic groups form complexes with metallic ions when with suitable reactive groups, such as carboxyls, hydroxyls and phenoxyls. Carboxyl groups play an important role in metal binding for both humic and fulvic acids (Alloway, 1995). These PHEs can be converted into their methyl forms, such as methylmercury by humic substances and bacteria (Sánchez Uría and Sanz-Medel, 1998). Methylmercury, for example, has high affinity to sulphydril groups, the organic components containing one sulphur atom. Sulphide groups in the sediments would also bind these organometallic complexes and are also responsible for the preconcentration of the methyl compounds in the sediments (Craig and Moreton, 1986).

3.12 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings that do not contain heteroatoms (any other atom than carbon (C) and hydrogen (H) and substituents) (Unlu *et al.*, 2010). They are highly lipophilic and have low solubility in water (Ke *et al.*, 2009). Polycyclic aromatic hydrocarbons are mainly formed by pyrolitic processes, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas, including for heating, combustion of refuse and vehicle traffic as well as natural carbonisation (Unlu *et al.*, 2010). The larger PAHs are less water soluble and less volatile and thus are mainly found in sediments and oily substances, as opposed to air although they are adsorbed on particulates that can be in suspension in the atmosphere. These can photodecompose when exposed to UV light from solar radiation and can react with pollutants such as ozone, nitrogen oxides and sulphur dioxide resulting in diones, nitro and dinitro PAHs and sulphonic acids, respectively (Ashworth, 2005). Unfortunately, PAHs are also carcinogenic, mutagenic and teratogenic which makes them a priority for concerned authorities (Unlu *et al.*, 2010).

There are more than 100 different PAHs amongst which 17 have been listed as priorities as hazardous to human health (carcinogenic, teratogenic and mutagenic). Figure 6 shows the chemical formulae and structures of the 17 PAHs (Agency for Toxic Substances and Disease Registry, 1995). The 17 PAHs were chosen for three reasons, namely, their higher toxicity compared to other PAHs, the higher potential human exposure to the PAH compared to others and finally, the amount of completed research conducted on these PAHs (Agency for Toxic Substances and Disease Registry, 1995).

There is an estimated input of 230,000 metric tonnes of PAHs released annually to the aquatic environment (Djomo *et al.*, 2004). Since PAHs are hydrophobic and have a strong tendency of sorption to sediments, they are persistent and are often difficult to remediate (Luthy *et al.*, 1997). Remediation strategies often involve mobilising agents, such as chemical surfactants (Thibault and Frankenberger, 1996), organic solvents (Jimenez and Bartha, 1996) and dissolved organic matter (DOM) (Rebhun *et al.*, 1996; Conte *et al.*, 2005; Conte *et al.*, 2001). Unfortunately, some of these mobilising agents can often be toxic to living organisms or to the environment which would negate any remediation endeavours (Ke *et al.*, 2003). Some researchers suggest that PAH degradation is increased by the addition of humic acid (Laor *et al.*, 1999; Fava *et al.*, 2004; Liang *et al.*, 2007), while others have reported contrasting results

where humic acids did not have any effects on PAH or even have a negative effect on the degradation of PAHs (Burgos *et al.*, 2000; Seibel *et al.*, 1996).

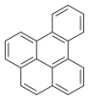
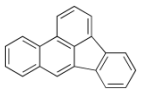
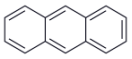
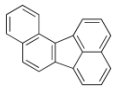
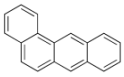
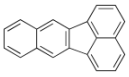
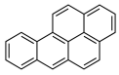
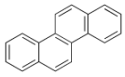
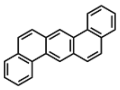
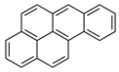
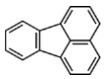
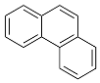
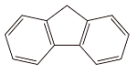
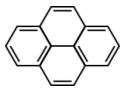
			Benzo[e]pyrene	$C_{20}H_{12}$	
Acenaphthene	$C_{12}H_{10}$		Benzo[b]Fluoranthene	$C_{20}H_{12}$	
Acenaphthylene	$C_{12}H_8$		Benzo[j]Fluoranthene	$C_{20}H_{12}$	
Anthracene	$C_{14}H_{10}$		Benzo[g,h,i]Perylene	$C_{22}H_{12}$	
Benzo[a]anthracene	$C_{18}H_{12}$		Benzo[k]Fluoranthene	$C_{20}H_{12}$	
Benzo[a]pyrene	$C_{20}H_{12}$		Chrysene	$C_{18}H_{12}$	
Dibenz[a,h]Anthracene	$C_{22}H_{14}$		Indeno[1,2,3-c,d]pyrene	$C_{22}H_{12}$	
Fluoranthene	$C_{16}H_{10}$		Phenanthrene	$C_{14}H_{10}$	
Fluorene	$C_{13}H_{10}$		Pyrene	$C_{16}H_{10}$	

Figure 6: Polycyclic Aromatic Hydrocarbons (Agency for Toxic Substances and Disease Registry, 1995).

PAHs can be biomagnified and bioaccumulated by micro-organisms which are responsible for the degradation of PAHs. Remediation using microbial processes has become the preferred method for remediation of sediments containing PAHs, as micro-organisms are the most effective and environmentally friendly way of treating the PAHs in these sediments (Ke *et al.*, 2010). The micro-organisms absorb, adsorb, degrade or store the PAHs which can be affected by various factors, such as pH, oxygen availability, population of micro-organisms, but mainly co-contamination (Ke *et al.*, 2010). Phenanphrene, for example, has been shown to increase the degradation of pyrene by bacteria (Tiehm and Fritzsche, 1995), while both these PAHs can be degraded by other bacterial species stimulated by naphthalene (McNally *et al.*, 1999). However, some researchers have found that the presence of some of the priority PAHs, for example, fluoranthene, can cause a lower effectiveness of the bacteria to degrade other PAHs

(Dean-Ross *et al.*, 2002). Most of the research on biodegradation and bioabsorption of PAHs have used bacteria or fungi as micro-organisms (Aksu, 2005; Bhushan *et al.*, 2000; Chauhan and Jain, 2000; Samanta *et al.*, 1999).

It is quite difficult to assess the reliability of any remediation strategy when there are so many factors affecting the effectiveness of the method or the behaviour of the PAHs. The latter can be affected by metals which can either decrease the efficiency of the bacteria due to metal toxicity (Aksu and Akpinar, 2001), even with very low concentrations, as reported by Amor *et al*. (2001). On the other hand, some researchers have found that some metals can stimulate microbial activity, for example low concentrations of Ni can enhance the effect of some bacteria (Gonzalez-Gil *et al.*, 1999). These opposing results show how complex the combined effects of metals and other constituents of sediments can have on organic pollutants.

3.13 FACTORS INFLUENCING BEHAVIOUR OF PHEs IN SEDIMENTS

There are several factors affecting PHEs in sediments. These parameters can be external, such as pH, temperature, conductivity, Redox potential, oxygen availability, or internal such as particle size, competition between ions, interactions between ions, ions affecting other ions or affecting external parameters.

3.13.1 pH

It has been well established that pH greatly influences adsorption of PHEs by zeolites. The problem that arises when considering mixed PHEs adsorption is that different PHEs are adsorbed at different pH. A change in pH can also bring about changes in chemical composition of compounds, or precipitation (Stylianou *et al.*, 2007), hydrolysis of the solids, degradation, dissolution and phase transformations (Rivera *et al.*, 2000). Querol *et al.* (2006) showed that an increase in pH favours metal hydroxide precipitation, especially for Fe and Al. Research on the effects of pH on several PHEs showed that although some PHEs such as Cr and Fe can be adsorbed effectively at low pH, they can also be adsorbed at higher pH by up to 100% with other PHEs when using absorbents such as zeolites (Hatje *et al.*, 2003). The optimum pH for heavy metal removal can be different for various PHEs, but in most cases the increase in pH caused by addition of zeolitic materials for example reduces the mobility of PHEs (Garcia-Sanchez *et al.*, 1999). Ag (I) for example is adsorbed at an optimum pH of 4 which is not the optimum pH for other PHEs (Akgul *et al.*, 2006). Research (Akgul et al., 2006) on adsorption of Ag on clinoptilolite have shown that although the optimum pH is 4, a

high adsorption rate still occurs at higher pH and thus in a mixed PHE situation, Ag would still be adsorbed when considering pH for other 'important' PHEs. Adding zeolites to sediments also bring about a change in pH which in turn accelerates the process of adsorption (Rivera *et al.*, 2000). The increase in pH when zeolites are added to sediments also favours polymerisation-precipitation of Cr for example, which in turn improved the efficiency of the zeolites to remove the PHEs compared to pure cationic exchange reactions (Basaldella *et al.*, 2007). Shibata and Seff (1997) also found that Pb absorption increases with increasing pH. Bentonite also absorbs Pb, but most efficiently at lower pH values. At lower pH, the Si attracts positively charged adsorbate ions by couloumbic forces. This negative charge density decreases as the pH increases and thus the adsorption on Pb decreases (Inglezakis and Loizidou, 2007). At higher pH values, the surface functional groups can dissociate, leaving anionic surface sites that can improve heavy metal adsorption and thus shows that higher pH increases metal removal. It can also be noted that the highest adsorption occurs at the isoelectric point of the adsorbent (Huang *et al.*, 2007). Zhang *et al*. (2007) also agreed that higher pH increases adsorption rates up to the alkaline level after which adsorption rate decreases and this is due in this case to ammonium being transformed into an electrically neutral form. Lin *et al*. (1998) also showed that Cd leaching is reduced with increasing pH. Furthermore, an increasing pH increases the soil Cd holding capacity by up to 3 times for one pH value increase. Zeolites can also affect pH and in most cases increases the pH by up to 4 pH values due to the hydrolysis of zeolites (Curkovic *et al.*, 1997). Although PHEs removal increases with high pH, many researchers have found that the efficiency of clinoptilolite, for example, decreases with pH values higher than 10. This is probably due to the formation of anionic hydroxocomplexes which have little affinity for cationic ion exchange sites in clinoptilolite (Vaca Mier *et al.*, 2001). Mahabadi *et al.* (2007) also showed that high pH values contribute to Cd immobilisation. An increase in soil pH contributes to immobilisation of PHEs by making the exchange sites in soil more reactive to metal binding, due to lower proton competition (Oste *et al.*, 2002a; Oste *et al.*, 2002b).

On the other hand, at very low pH, the decrease in heavy metal uptake is mainly due to competition with H^+ ions. Clinoptilolite in this case will tend to neutralise the solution by H^+ uptake (Inglezakis *et al.*, 2003; Ajmal *et al.*, 2001).

3.13.2 Redox potential

Redox potential is one of the most important variables to consider when studying sediments after pH (Forstner and Calmano, 1998). The Redox potential is measured in volts for the affinity of a substance for electrons (Sparks, 1999). Electronegativity values are compared to hydrogen, which is given a value of zero. If the substance has higher electronegativity compared to hydrogen, it will have a positive Redox potential and capable of oxidising, whereas substances with less electronegativity with regards to hydrogen will have negative Redox potential and thus capable of reducing. Kelderman *et al*. (2007) tested the effects of Redox potential on binding of PHEs. With a gradual change from negative to positive Redox potential, they found that PHEs were released by up to 37% through oxidation of sulphides for example, which would release PHEs associated with them. This was mainly due to the oxidation of the heavy metal-sulphide bindings. Another important piece of research on Redox potential and sediment by Caplat *et al*. (2005) showed that dredged sediments were characterised by a high proportion of reducible materials (oxihydroxides, oxides) and Redox potential below -200 mV. This potential shows early chemical, physical and biological changes that sediments undergo after initial deposition (diagenetic processes) such as sulphate reduction, which may lead to growth of metallic sulphides (Kersten and Forstner, 1986), considered as a sink for trace metals (Douglas and Adeney, 2000).

3.13.3 Particle size and remediation

Particle size is an important factor to be considered when studying PHEs and more importantly when studying zeolites. It has been well established that PHE concentrations are higher in the finer sediments, especially clays (Herngren *et al.*, 2006). It has been shown by various researchers that there is a linear relationship between organic matter and PHEs, showing that fine particulates may contain higher organic carbon and higher concentrations of PHEs (Herngren *et al.*, 2006; Warren *et al.*, 2003). Zeolites are also affected by their particle size as the finer the zeolite, the more PHEs it will absorb due to the larger surface area of the adsorbent (Zorpas *et al.*, 2002; Inglezakis and Loizidou, 2007). It has been shown by other research (Inglezakis and Grigoropoulou, 2004), that decreasing the particle size of clinoptilolite by half, can increase the removal efficiency by a factor near to 2. However, the research also demonstrated that decreasing the particle size also resulted in higher flow resistance in column reactors which can decrease the overall removal efficiency in column reactors.

Another issue with mixed PHEs removal by zeolites is the way the zeolites interact with each other and at the same time being affected by external parameters. Cr (VI), for example, can interact with both Pb and Zn to form anionic complexes which significantly reduce absorption by zeolites (Vaca Mier *et al.*, 2001). Unfortunately when considering zeolites in soil remediation, the effectiveness of the zeolites to absorb PHEs also means that some important nutrients needed by plants are also immobilised and thus more research needs to be done in the agricultural sector (Baydina, 1996) so that zeolites can selectively reject important ions that are needed by plants. Alternatively, when considering only remediation, and especially contaminated sites or canal sediments, the effectiveness to absorb PHEs is crucial.

Leaching of PHEs from contaminated soils is a major problem that has to be considered when studying remediation. Zeolites are also often used to immobilise these PHEs and reduce leaching, especially for PHEs such as Co, Cu, Ni and Zn, which can also be toxic to human health at high concentrations. The alkalinity brought by the zeolites causes precipitation of insoluble phases (Querol *et al.*, 2006). Lin *et al*. (1998) also showed that zeolites can reduce Cd leaching by up to 99% by adding zeolites to soils or sediments. For sandy and loamy soils, adding zeolites effectively reduces the average particle size, whereas in clay soils, the zeolites arguably improve the overall physical properties of the soil (Lin *et al.*, 1998; Mahabadi *et al.*, 2007). With smaller particle size, the availability and accessibility of exchange or adsorption sites are improved. Even if a site is available, the cation movement to the site can be characterised by a degree of difficulty, generally different for each site (Inglezakis and Loizidou, 2007). Even then, since the path length of the ions to the exchange sites is shortened, a noticeable improvement in the removal efficiency of the adsorbent is noticed (Park *et al.*, 2002). Ajmal *et al*. (2001) and Mahabadi *et al*. (2007) showed that the finest clinoptilolite (mesh size 200 µm) absorbs about 92% of Cu (II) compared to other larger mesh sizes.

3.13.4 Effect of concentration

Various researchers (Inglezakis *et al.*, 2002; Park *et al.*, 2002; Sprynskyy *et al.*, 2006; Wang *et al.*, 2006) have shown that initial concentration of heavy metal in solution is important when considering sorption by zeolites. Dilution of solution often leads to an increase in the volume treated. This can be attributed to the increase of selectivity in ion exchange by dilution of the solution. This is commonly known as the concentration-valency effect, where the valences of the exchanging ions have a strong effect on the ion exchange equilibrium (Inglezakis and Grigoropoulou, 2004). Similar results have been found by Akgul *et al*. (2006) for the

adsorption of Ag by clinoptilolite. Increasing the initial concentration of Ag in the solution brings about a decrease in overall percentage adsorption. This is also due to the saturation of adsorption sites available on the zeolites. The plateau at which the highest adsorption rates occur before declining is the maximum adsorption capacity of the zeolites (Akgul *et al.*, 2006). The maximum adsorption capacity is different for different PHEs and is also dependent on the Si/Al ratio, as a lower Si/Al ratio has greater removal capacity due to greater concentration of aluminol surface groups (Shevade and Ford, 2004).

3.13.5 Dissolved Organic Matter

Dissolved organic matter plays an important role in soil and sediment processes. Many researchers have found that sediments with higher organic matter have higher concentrations of PHEs (Oste *et al.*, 2002a; Cook and Parker, 2003; Luo *et al.*, 2008). Organic matter has a high cation exchange capacity and thus is an important sorbent for PHEs, resulting in organic-contaminant complexes (Alloway, 1995). Natural organic matter consists of three main constituents: humic acid, fulvic acid and humin. Humic acid is soluble at higher pH and precipitates at pH 2, fulvic acid is soluble whether the solution is acidic or basic and humin is insoluble at all pH values. Humic substances can have various functional groups, for example ester, carbonyls, carboxyls and phenolic hydroxyls and have different molecular weight, acidity and cation exchange capacity in the order; humin > humic acid > fulvic acid. Sauvé *et al.* (2000) illustrated the importance of organic matter in sediments in the form of metal-organic complexes. However, it should be noted that the effect of organic matter on the solubility of PHEs in sediments is affected by physical and chemical factors, such as pH and calcium (Ca) concentration. Ca can have a bilateral effect on organic matter. Firstly, Ca can cause the dissolved organic matter (DOM) to coagulate and thus reduce the amount of DOM, consequently reducing the concentration of dissolved metals. Conversely, Ca can also compete for adsorption sites on the solid phase, like other similar cations, thus resulting in an increase in the solubility of some metals.

Several researchers have investigated the effects of organic matter on mobility of PHEs and the results varied, as illustrated by Saada *et al.* (2003), Tessier *et al.* (1996) and Christensen (1998), who concluded that humic acids decreased the mobility of PHEs. Other researchers found completely opposing results, where organic matter enhanced mobility of PHEs (Redman *et al.*, 2002; Sauvé *et al.*, 2000) in natural waters. The major difference in results is due to the differences in heterogeneity of the organic matter under investigation.

Humic acid can either increase or decrease mobility of PHEs, depending on whether it is in solution, where it enhances mobility as it has a negative charge, or adsorbed onto the solid phase, where mobility is decreased (Shen, 1999). Sorption onto the solid phase depends on the surface charge and since Al and Fe hydroxides have a positive charge; as they are basic and accept protons from solution; they are favoured to silicon dioxide; which is acidic and releases protons above pH 3-4 and is negatively charged. Consequently, Al and Fe hydroxides will form complexes with humic acid functional groups (Shen, 1999). pH can have a strong effect on organic matter and solubility of PHEs. Humic acid can be strongly bound to mineral surfaces at pH 2.5 or below and competition for protons can result in desorption of metals (Kedziorek and Bourg, 1996). In addition, Spark *et al*. (1997) illustrated the effect of pH on different PHEs. Zn, Cu and Co undergo maximum sorption to humic acids at pH 6, whereas Cd is sorbed at pH 8. Other factors, such as particle size, can also affect organic matter as the latter is associated mostly with the finer clay and silt particles (Cheshire *et al.*, 2000; Christensen, 1998). The organic matter in sediments mainly occurs as coatings on the hydroxide coatings on the individual mineral particles (Tessier *et al.*, 1996).

Organic compounds when present in soils can hinder metal removal efficiency of the zeolites, as they form organometallic complexes with the PHEs which cannot penetrate the zeolite exchange channels (Vaca Mier *et al.*, 2001). Similar results have been found by Singh *et al*. (2006), who found that Pb removal can be decreased by the presence of organic ligands, which generally tend to have complexation reactions such as metal-ligand ion pair, soluble metal-ligand complexation and chelations.

3.13.6 Effect of chloride and sulphides

Sulphides play an important role in the bioavailability of PHEs in sediments and thus the subsequent potential remediation of these sediments. Sulphides are a vital component to consider when studying anoxic sediments, as anoxic conditions bring about high production of hydrogen sulphide mediated by microbial activity (Naylor *et al.*, 2004) and the high organic matter found in canal sediments (Stephens *et al.*, 2001b). Most of this hydrogen sulphide is reoxidised but the rest reacts with other PHEs to form sulphide minerals, such as pyrite (FeS_2), sphalerite (ZnS), galena (PbS), marcasite (FeS_2) and amorphous iron sulphide (FeS) (Caille *et al.*, 2003; Brennan and Lindsay, 1996). Other metals coprecipitate and are absorbed on FeS (Morse and Luther, 1999). There are different possible reactions that can occur in the presence of FeS. A common sequence is metals absorption and inclusion, metathesis

(AX+BY→AY+BX) or metal exchange reactions, pyrite formation and inclusion of metal into pyrite. Moreover, metal sulphides are usually insoluble, which limits the bioavailability of the metals in sulphidic sediments (Naylor *et al.*, 2006). The major sulphide component in most sediment is FeS due to the high abundance of Fe oxyhydroxides and their ease of reduction to Fe(II) in anoxic conditions (Zaggia and Zonta, 1997). Amorphous FeS is the most soluble sulphide and thus other metals can displace Fe to form more stable sulphides (Cooper and Morse, 1999). Sulphides are very dependent on Redox changes (Naylor *et al.*, 2004) and dredging or any other activity that might bring about rapid oxygenation and thus fast sulphide oxidation. More soluble compounds could thus be formed, but such processes should be avoided, as oxidation could have a detrimental effect on the biota of the canals (Perin *et al.*, 1997a). Unfortunately, there is little research that has actually examined the quantitative distribution of the PHEs bound to carbonates, Fe-oxides, Mn-oxides, organic matter and the sulphides in anoxic sediments (Yu *et al.*, 2001).

METHODOLOGY

CHAPTER 4

"Do not go where the path may lead, go instead where there is no path and leave a trail" -Ralph Waldo Emerson.

CHAPTER 4

METHODOLOGY

4.1 INTRODUCTION

Characterisation is crucial when considering remediation of canal sediments, as PHEs in the sediments can be associated with the organic fraction, Fe and Mn oxides and/or carbonates. Such associations can be determined using sequential extraction methods, but there are also other variables that are relevant to secondary processes operating in dredged canal sediments. It thus follows that other proxy methods are required to understand both the nature of the sediments themselves and processes operating in the sediments after dredging. Figure 7 shows the range of analytical techniques used in this research covering every aspect of the physical and geo-chemical characterisation of the sediments.

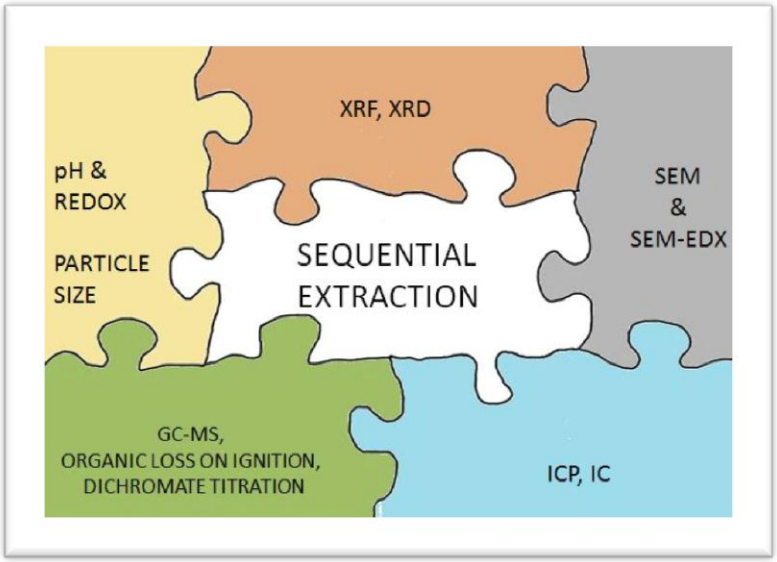


Figure 7: Methods used in this research (pH & Redox, Particle size, X-Ray Fluorescence, X-Ray Diffraction, Scanning Electron Microscope, Energy Dispersive X-ray, Inductively Coupled Plasma-Optical Emissions Spectroscopy, Ion Chromatography, Gas-Chromatography Mass Spectrometry, Organic Loss on Ignition and Sequential Extraction).

Preliminary results from the pilot study have shown that there was a mass balance difference after the zeolites treatment (PHE concentrations lost from sediments did not match percentage concentrations sorbed onto zeolites). As discussed in Section 2.4.7, this could be due to PHE oxidation, binding to pyrite and the mobility of the PHEs resulting from oxygenation as sediments are removed from the canal. Such processes probably occur within the sediments and pore water chemistry, between the time of the dredging operation and disposal and form

the focus of this research. Remedial strategies do not currently take these processes into account, therefore any remediation endeavour on these sediments may be unsatisfactory if these secondary processes are not fully understood. Information on the sediments *in situ*, such as the concentrations of PHEs, are not relevant to this research, which attempts to clarify sediment characterisation and secondary processes post-dredging operation and prior to potential remediation.

4.2 SITE DESCRIPTION

The West Midlands area is well known for its industrial heritage, as discussed in Section 3.9.2. The three sites used in this research project were recommended by BW as sites that have not previously been dredged and potentially contain the highest contamination levels and high PHEs concentration (Proffitt and Beckwith, 2008). Figure 8 shows the relative locations of the 3 sampling sites.

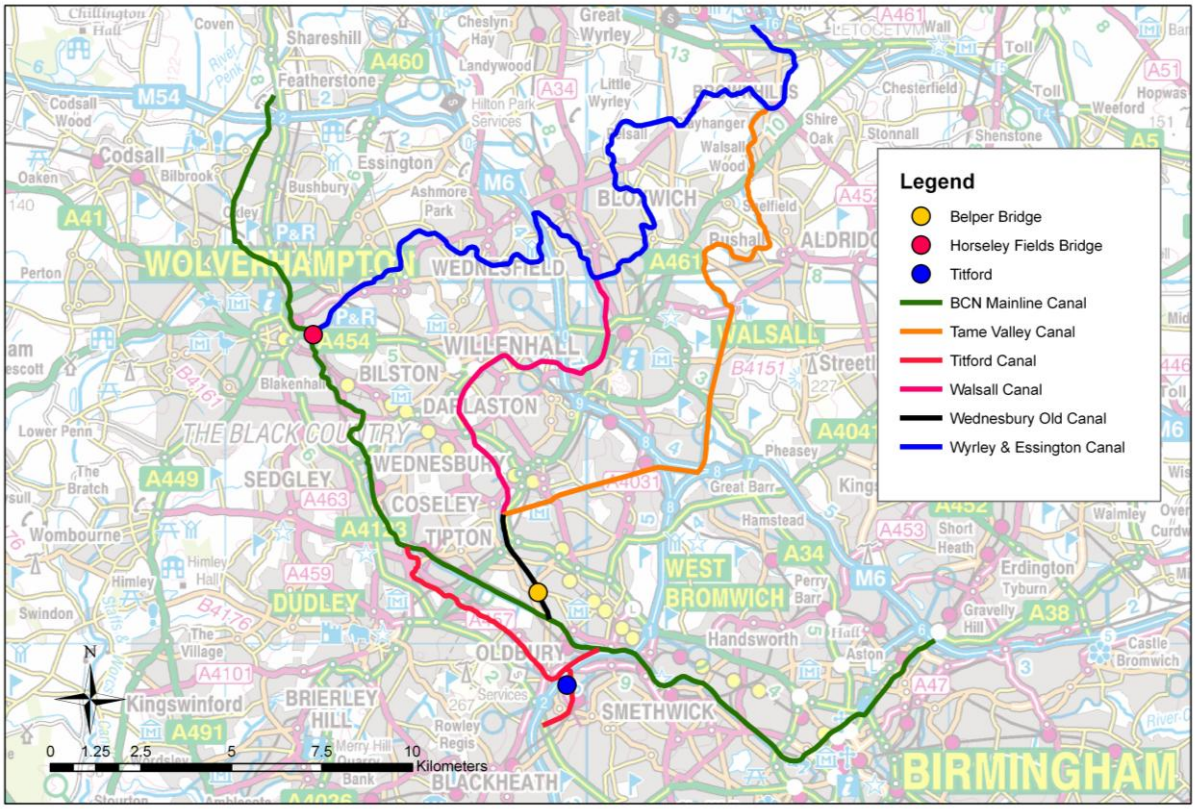


Figure 8: GIS map of Birmingham Canal Navigations (BCN) and connecting canals between Wolverhampton and Birmingham and sampling sites.

The first location was Belper Bridge (SO 98653 91415) on the Wednesbury Old Canal, which is a connection from the Walsall Canal to the Birmingham Canal Navigations. This area was

the location of intensive industrial activity in the 18th and 19th centuries. The second site was Titford Canal in Oldbury (SO 99449 88850). Canal sediments in this area are well known for high organic content, as coal tar production was one of the main industrial activities during the Industrial Revolution. The third sampling site was Horseley Fields Bridge in Wolverhampton (SO 92439 98539) at the junction between the Wyrley and Essington Canal and the Birmingham Canal Navigation main line. This area of Wolverhampton has a well-established industrial legacy, as described in Table 6 (Chapter 3).

4.3 SAMPLING OF SEDIMENTS AND EXPERIMENTAL SETUP

At each of the three locations, random bulk samples were obtained with a Bunce Gulley sedimentary grab (Plate 3a) which allows sediment to be retrieved from approximately 25-30 cm depth. Bulk samples were then placed in plastic boxes (dimensions outlined in Section 2.4.2), sealed and allowed to settle for up to 2 weeks. Each site provided 10 different sets of bulk samples from a 10 m stretch of canal, to minimise spatial variations. The sediments were allowed to settle and consolidate in the box so that the sediment occupied approximately 80% of the box volume (Plate 3b). The boxes were kept in the light to mimic conditions that the sediments would go through in the natural environment after they are dredged. Although glass (inert material) would have been the preferred storage material for the tanks, it was unavailable for this research. The supernatant on top of the sediments (once the sediments settled) was siphoned off, measured with a measuring cylinder and kept for ICP and IC analysis. Once the sediments settled in the tank, various analytical techniques were used to characterise the sediments replicating what happens on a larger scale (dredging barges) between the time they are dredged and the time of disposal.

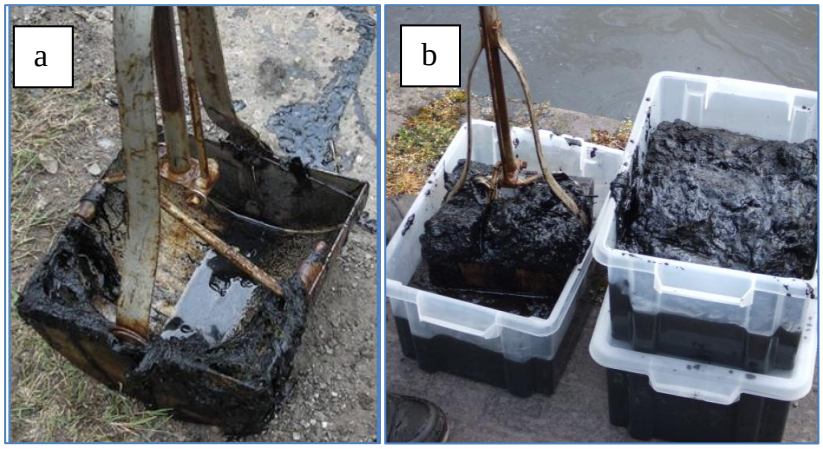


Plate 3: a) Bunce Gulley sediment grab used for sampling and b) tanks filled to 80% of their capacity.

4.4 METHODOLOGY SEQUENCE AND NUMBER OF SAMPLES FOR EACH ANALYTICAL TECHNIQUE

To achieve thorough characterisation, a number of samples were chosen for each analytical method. Factors such as the importance of the analysis (sequential extraction, for example, was considered more important compared to a proxy analysis such as XRF or SEM), availability of specific analysis and finally cost of analysis were taken into consideration. The methods shown in Figure 9 show the different analytical methods and the sequence in which the analysis was conducted. Each of the analytical methods covered one aspect of the sediments; ICP and IC for the pore water, XRF and XRD for the sediment chemistry, LOI and GC-MS for the organic phase, SEM-EDX for microscopy and elemental analysis, particle size for the physical properties, pH and Redox for the electrochemical properties and Sequential Extraction for an overview of the sediment fractions.

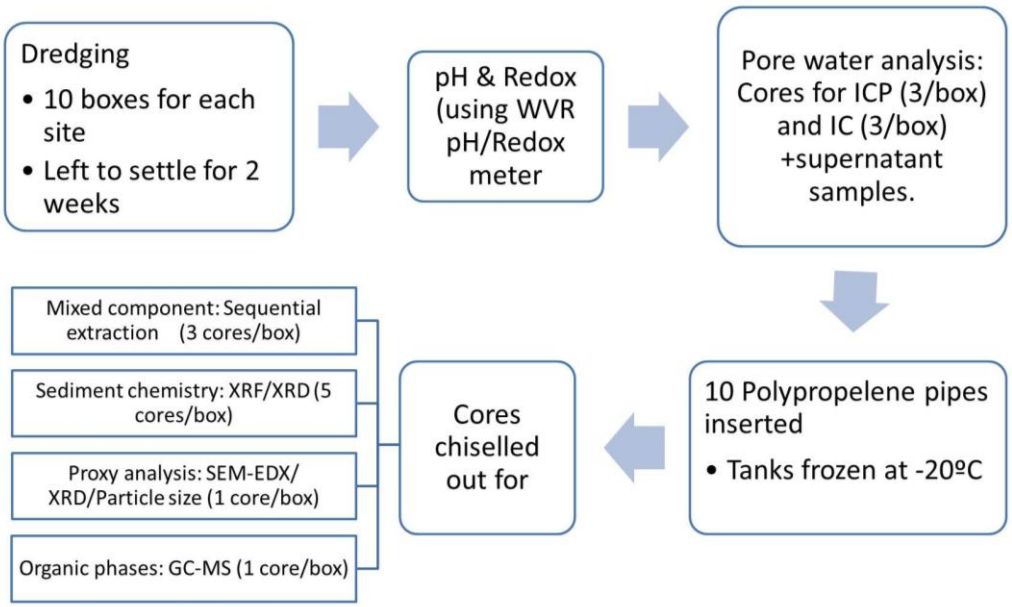


Figure 9: Sequence of analytical procedure.

Table 8 shows the number of samples collected for each type of analysis. The three samples for each core mentioned in the table were, top, middle and bottom sections and the supernatant was, additionally, analysed for the pore water analysis. The sediments had high water content which would facilitate settling of the sediments with time, making the tanks not homogenous from top to bottom and analysing at three different levels in the tanks ensured that the physical and geochemical characteristics and processes occurring in the sediments are all investigated.

Table 8: Number of samples/readings for each analysis

Analysis:	No. of samples:	Notes:	Total /analysis:
ICP	3 samples /core + supernatant	3 samples x3 cores +1 supernatant= 10/tank. (100 for each site)	**300**
IC	3 samples /core + supernatant	3 samples x3 cores +1 supernatant= 10/tank. (100 for each site)	**300**
XRF	3 samples/core	3 samples x 5 cores= 15/tank (150 for each site)	**450**
SEQ-EXT	3 samples/core X12 cores/site	14 extractants/sample. 36 samples/site= total 108 samples.	**1512**
GC-MS	3 samples/core	2 solvents: hexane and ethyl acetate/sample= 6 samples/site.	**18**
Particle size	3 samples/core	9 samples/site	**27**
XRD	3 samples/core	9 samples/ site	**27**
pH	4 corners+ centre	6 intervals (30 replicates/tank= 300/site)	**900**
Redox	4 corners+ centre	6 intervals (30 replicates/tank= 300/site)	**900**

4.4.1 Frozen cores for various analyses

Ten PVC pipes were inserted at different locations in the sediment tanks after the six cores for ICP and IC were taken out. The cores were inserted in a specific configuration for all tanks for all sites to cover a maximum range in the tank, as shown in Figure 10. The tank was then frozen at -20 °C. A temperature of -20ºC was used for sample storage to limit abiotic processes, such as volatilization, sorption, chemical reaction and microbial degradation, which were identified as the contributors to analyte losses during storage of soil as well as aqueous samples (Rost *et al.*, 2002). Freezing also allows the samples to be prepared more efficiently and avoid contamination. The three samples from each core were obtained more precisely as the frozen cores were cut exactly at 4 cm intervals. Once frozen, the cores were chiselled out of the structure (Plate 4) and were cut into three equal sections of 4 cm, top, middle and bottom and used for the different analyses described in Section 4.7-4.9.

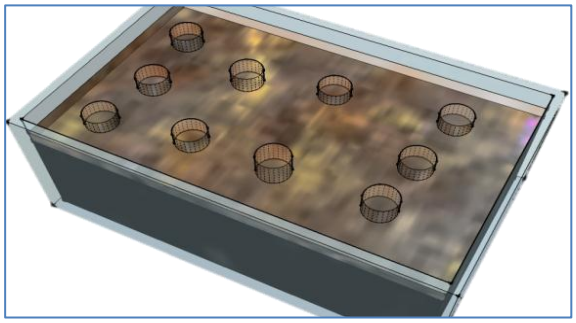


Figure 10: PVC pipes location in tanks.

Plate 4: Cores extracted from frozen tanks.

4.5 ELECTROCHEMICAL CHARACTERISATION

4.5.1 Redox and pH

pH and Redox were measured after the sediments settled in the tanks at different levels in the sediment tanks to measure variations with depth. A handheld pH meter, the WVR pH-100, was used with a pH probe (range of 0-14 ± 0.01) and a Redox probe (range of -1999 to 1250 mV ± 1mV). The probe was carefully inserted in the tank and clamped to a ruler which was used to measure more accurately the depth at which readings were taken. Readings were taken from the top oxidising layer to the bottom of the tank at 2 cm intervals. The probe was then changed to an Oxidation Reduction Potential (ORP) probe and the same procedure was followed for Redox measurements. Other methods to measure pH and Redox, such as shaking sediment samples with deionised water and centrifuging, would not have been effective, as the pH and Redox potential would have changed with oxygen availability. The readings were repeated at five different locations within each tank (Figure 11) for both pH and Redox.

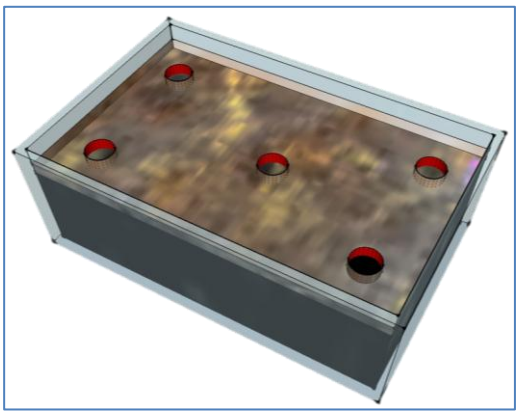


Figure 11: pH and Redox analysis sample points- 6 readings from the surface to the bottom of the sediment tank.

4.6 LIQUID PHASE CHARACTERISATION: ELEMENTAL AND IONIC CONCENTRATION IN PORE WATER

Before freezing, six cores were then taken out from random locations in the tank using a PVC pipe (40 mm in diameter and 20 cm long). The 12 cm cores were then subdivided into three equal segments. The sediment sections were transferred separately into centrifuge tubes and centrifuged for 30 minutes at 2000 rpm. Once centrifuged, the pore water from each segment was decanted and filtered using 0.2 µm filters attached to a syringe. The pore water from three of the cores were analysed using Inductively Coupled Plasma (ICP) analysis (4.6.1), whilst the pore water derived from the other three cores were analysed using Ion Chromatography (IC) analysis (4.6.2).

4.6.1 Analysis using Inductively-Coupled Plasma (ICP)

The ICP machine, SPECTRO CIROS CCD solid state detector ICP-OES (Plate 5) was used to analyse pore water samples. This instrument has continuous 1st Order wavelength coverage from 125 nm to 770 nm wavelength region and has sensitive and interference-free lines for a wide variety of elements. The samples were analysed for As, Ca, Cd, Co, Cr, Cu, Mg, Na, Ni, Sb, Se, Sn, Sr, Ti, V, Zn, Ba, Mo, Mn, Pb, S, K, P, Si, Fe, Al and Hg. The ICP has a limit of detection of 1 µg/kg.

Plate 5: Spectro Ciros CCD- Inductively Coupled Plasma with Auto Sampler attachment.

4.6.2 Analysis using Ion chromatography (IC)

IC using the Dionex ICS 90 was used to determine the following anion complexes: sulphates, chlorides, sulphides, phosphates, bromides, nitrates and nitrites. Analysis involves using

continuous chemical suppression and thermally stabilised digital conductivity detection to give fast, accurate determinations of common anions and cations over broad concentration ranges. The Dionex ICS 90 is easy to operate, quick to equilibrate, and fully automated with Chromeleon® SE software. The limit of detection of the Dionex ICS 90 is 0.01 mg/l.

4.7 SOLID PHASE CHARACTERISATION

4.7.1 Particle size sample preparation

Sediment samples for particle size analysis had to be prepared before analysis at Coventry University, following the method used by the manufacturers of the Malvern Mastersizer and Booth *et al*. (2005). Three cores from each site (nine cores in total) were subdivided into three (top, middle and bottom) and were oven dried at 40 °C for 24 hours. The sediments were then disaggregated in a crucible and sieved using a 2.0 mm mesh size followed by a 1.0 mm mesh size. The sieved sediments were then treated with hydrogen peroxide for 20 minutes on a hot plate, to remove organic constituents. Once the mixture had a paste texture, a few drops of sodium hexametaphosphate (40 g in 1 litre of distilled water) was added to aid deflocculation. The samples were then ready for particle size analysis. They were put in an ultrasonic bath just before analysis to ensure that the clay particles did not adhere and subsequently affect the particle size analysis results.

4.7.2 Analysis using Granulometer (MALVERN MASTERSIZER)

Particle size for sediment samples was measured using a granulometer. The latter uses laser dispersion to measure accurately the range of particle sizes in a particular sample. There are two lenses on the Malvern Mastersizer granulometer, one with a range of 4-2000 µm and the other one with a range of 0.1-80 µm. The software then combines the two data sets to give a normal distribution of the particle size in the samples. The software also provides information on the distribution and statistical breakdown of the various component sizes in the sample. From this set of data, the percentage of clay, silt and sand can then be determined.

The granulometer was equipped with a dispersion unit, where the prepared sample was fed into the granulometer. The unit used ultrasonic vibration to break down any residual inter-particle bonds in the water in the dispersion unit. Once the lens was aligned, the sample and a few drops of solvent (to dissolve the clay bridges) were added slowly until the optical density efficiency, which is optimum at around 15-20% (according to manufacturer's guide) was achieved. Following analysis and data collection, the small volume sample dispersion unit was

drained and thoroughly cleaned with deionised water and the lens was realigned to analyse the next sample. Each sample was analysed four times and the mean was computed by the software giving the full range of particle size between 0.1-2000 µm. The software routine used to analyse these samples (SOIL2) was the one advised by Malvern personnel as being the most appropriate setting for analysing samples consisting of mixtures of optically dissimilar materials (Booth *et al.*, 2003).

4.7.3 Microscopic analysis

Microscopic analysis was used as a proxy to visually investigate the canal sediments at high magnification and to characterise the chemical composition of the sediments using the EDX. Scanning electron microscopy has been used to explore the petrography of sediments in canal sediments (Large *et al.*, 2001) regarding the different minerals and associations that occur in these sediments. A frozen core (see Table 8) was sectioned into three equal segments (top, middle and bottom) and spread on petri dishes and left to air dry in fume cupboards. Once dried, the samples were disaggregated and bagged for Scanning Electron Microscope (SEM) (EVO 50, Zeiss) analysis, which was attached to an Energy Dispersive X-ray spectroscopy (EDX) (Oxford Instruments, Incax-sight) for elemental analysis.

The carbon stubs were aligned with the electron beam in the scanning electron microscope and samples were analysed under vacuum. Several methods were used in the preliminary study and the best results were found to be; EHT 20.00kV, WD 8.5 mm and a backscatter detector QBSD which highlights the PHEs in the sediments. Figure 12 shows samples analysed without and with the backscatter detector. The backscatter detector is used when samples have high organic content (20-30%), which mask different and varying compounds in the sample. Thus small compounds or elements highlighted in the sample by the detector are more easily analysed. Preliminary tests have shown that without the backscatter detector, all the analyses showed similar composition mainly consisting of organic matter. On the other hand, with the detector, only the highlighted parts were analysed using the EDX.

The powdered samples were mounted on carbon stubs and gold coated if necessary (when EDX results showed interesting results) for imaging purposes. The gold coating was used only after EDX analysis as it interferes with the EDX results, and the general focus on the SEM. Nonconductive specimens tend to charge when scanned by the electron beam which can cause scanning faults. Gold is a conductive material often used for coating which prevents the

accumulation of static electric charge on the specimen during electron irradiation. The stubs showing associations of PHEs were subsequently gold coated for imaging.

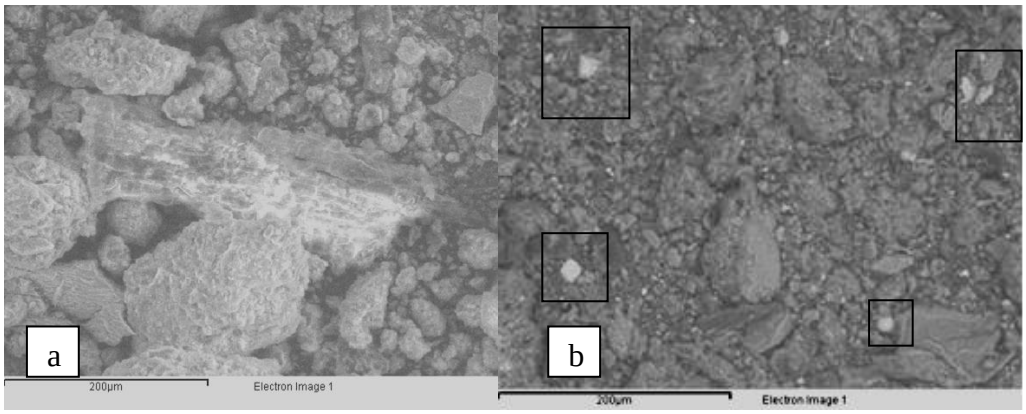


Figure 12: a) Scanning Electron Microscope image without backscatter detector showing the whole sample in grey and b) image with back scatter setting highlighting PHEs, lighter, brighter clusters on grey background.

4.7.4 X-Ray Fluorescence

Please refer to Section 2.4.4 and 2.4.5 for sample preparation and analysis for X-Ray Fluorescence Spectroscopy. The same sample preparation protocol (Section 2.4.4 and 2.4.5) was followed for the characterisation part of the research. Five cores were taken from each tank for XRF analysis. The samples were analysed for the full range of elements detectable by the XRF (Plate 2).

4.7.5 Analysis using X-Ray Diffraction

X-Ray Diffraction (PW1729 X-Ray generator, Philips) (Plate 6) was used to analyse chemical compounds in the sediments. Elemental concentrations (XRF) over 5% produce the most accurate results and although 5% is not expected for many elements, XRD was still used to obtain an overview of the types of minerals present in the sediments, as XRD was used as a proxy analysis to complement sequential extraction results. Nine samples from each site were used for XRD (Table 8). Like XRF, XRD has the advantage of being non-destructive, relatively cheap and detects a large range of minerals. Minerals analysed consist of crystalline structures comprised of an internal structure in a precise way (consistent for all crystals in the mineral) (Glusker *et al.*, 1972). X-rays are bombarded on the samples and are diffracted by the crystal structure at different angles. A diffractometer is used to measure the angles of diffraction which allows for qualitative identification (Christian and O'Reilly, 1986). The data given for each reflection is the scattering angle (2θ) and the intensity for each reflection. Samples with the highest percentage concentrations from the XRF results were used for the

XRD analysis and in order to achieve maximum efficiency in results, sample powder was used instead of discs, as the Licowax in the discs can interfere with the X-Rays.

Plate 6: PW1729 X-Ray generator, Philips X-Ray Diffraction instrument.

4.8 ORGANIC PHASE CHARACTERISATION

4.8.1 Organic loss on ignition

The 27 samples (see Table 8) were dried at 40 °C for 24 hours in crucibles and then weighed. They were then transferred to the oven pre-heated at 500 °C for two hours. They were left to cool down in a decicator which removed all the moisture. They were then weighed again to find the dry weight after burning. The weight loss on ignition was then expressed as a percentage organic loss.

$$\textbf{LOI:}\ \frac{m_b - m_a}{m_b} \times 100\%$$

Equation 1: Organic Loss on Ignition.

Where; m_a : mass of sample after ignition (g), m_b: mass of sample before ignition (g).

4.8.2 Gas Chromatography-Mass Spectrometry (GC-MS) sample preparation

18 samples for GC-MS were prepared using Soxhlet extraction (Figure 13) - a reflux system used to extract organic compounds from samples using a wide range of solvents. A 3 gramme sample was measured and placed in a thimble, which was then placed in a distillation arm. The latter was connected to a round bottom flask containing the solvent (hexane and ethyl acetate used separately) and at the top end connected to a condenser unit. This apparatus construction

was replicated for a second solvent for the same sample. The two solvents used were hexane and ethyl acetate. Hexane is a non-polar solvent and ethyl acetate is a polar solvent and since organic content of the sediments is unknown, both the solvents had to be used. The apparatus construction was left for 12 hours so that the reflux of the solvents through the samples could be repeated several times. The samples were then pre-concentrated using a Rotavapor Buchi R-200 and the dry residue was re-dissolved in 5 ml ethyl acetate purum (Sigma-Aldrich, purity >99.5%). A 1 µl solution was then used for GC-MS analysis. The same procedure was repeated for the hexane extract and the dry residue was then redisolved in 5 ml anhydrous hexane (Sigma-Aldrich, purity > 95%). One µl of this solution was used for GC-MS analysis. Analyses of samples were performed on GC-MS, Varian Star 3400 CX, linked to Mass Spectrometer Varian Saturn 2000 working as detector. The instrument during analysis was operated in nonisothermal mode with a temperature profile of 55 °C (2 minutes), then Ramp 1 at 10 increasing to 150 °C, Ramp 2 at 3 °C/min to 260 °C and kept at 260 °C for 10 minutes. The trap temperature for the MS was 220 °C (axial modulation voltage 4.0 V and emission current of 10 microamps).

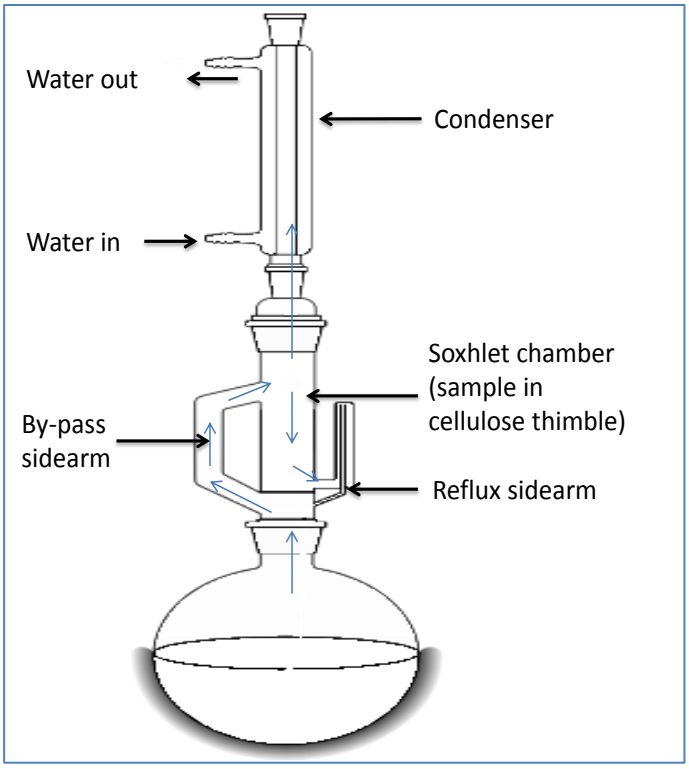


Figure 13: GC-MS sample preparation column apparatus construction with path of solvent shown in light blue arrows.

4.8.3 Analysis using Gas Chromatography- Mass Spectrometry (GC-MS)

The 6 samples, after being refluxed for 12 hours, were left to cool down, bottled and labelled. They were then sent to two laboratories, School of Applied Sciences, De Monfort University, Leicester for the first samples and SAL laboratories, Manchester, for the rest of the samples, for GC-MS analysis where the organic content of the samples were quantified and characterised. The results from both laboratories were used only for identifying the different organic compounds and not for quantifying, as quantifying would require a more extensive set of data which due to financial limitations could not be done.

4.9 MULTI-COMPONENT CHARACTERISATION

4.9.1 Sequential extraction

The different subsections (top, middle and bottom) of one core from each tank, were then analysed using the Chemometric Identification of Substrates and Element Distribution (CISED) sequential extraction procedure developed by the British Geological Society (BGS) (Wragg and Cave, 2009b) for the associations of PHEs to different phases in the sediments.

The extraction vessels used were Whatman Vectaspin 20 polypropylene centrifuge tubes with filter inserts (Anopore Plus), as shown on Figure 14. The filters used were inorganic Anopore membranes with a glass fibre pre-filter with a membrane pore size of 0.45 µm. Two grammes of the air-dried samples were weighed into the filter tube inserts. Aliquots of 10 ml extractant were then added to the filter insert and the tube was then centrifuged for 10 minutes at 1034g (2400 rpm). This speed was selected as it is lower than the maximum capacity of the Vectaspin membrane (2700 rpm). The resultant leachate was collected from the centrifuge tube and stored for ICP-MS analysis. The filter insert was then filled with the next extractant and the same procedure was repeated. The extractants used during the experiment were deionised water, 0.01, 0.05, 0.1, 0.5, 1 and 5 M *Aqua Regia*.

Table 9: Extractant molarity and volume of *Aqua Regia* used for preparation of each extractant

Extractant molarity (M)	**0.01**	**0.05**	**0.1**	**0.5**	**1**	**5**
Volume (ml) of *Aqua Regia* for 500ml deionised water	0.42	2.08	4.17	20.83	41.67	208.33

The extractants were prepared using 30% nitric acid and 70% hydrochloric acid. The acids were mixed to make up 300 ml of concentrated *Aqua Regia* which was then used to prepare the

different extractants with increasing molarities, as shown in Table 9. For the 0.1, 0.5, 1 and 5 M acid extracts, 0.25, 0.50, 0.75 and 1 ml, respectively, of hydrogen peroxide (H_2O_2), were also added to each extractant before making up to 10 ml volume. The addition of H_2O_2 was added to re-dissolve any precipitated organic matter.

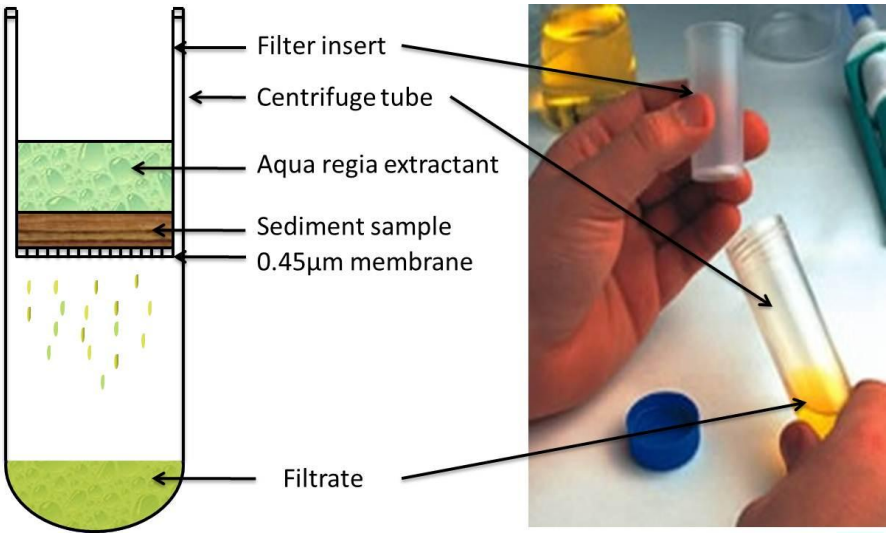


Figure 14: a) Vectaspin Anopore 20 centrifuge tubes showing extraction procedure and b) filter insert.

The CISED method has the advantage of being non-destructive, the sample remaining in the filter is thus ready for the next sequential extraction step reducing errors that might arise during transfer of sample involved in other sequential extraction procedures (Santamaria-Fernández *et al.*, 2006). The CISED extraction method also has the advantage of being quick, as up to 16 samples can be analysed at the same time depending on the centrifuge machine being used. Moreover, the contact time between reagent and the solid is short, thus minimising re-absorption problems (Cave *et al.*, 2004). The results are not methodologically defined and thus reflect the true physico-chemical properties of the sediment. Moreover, the method is the same for all elements and thus comparison of data and quality control between laboratories was simplified (Cave and Wragg, 1997). *Aqua Regia* being the only extractant used also means that the experimental procedure is also simplified. On the other hand, *Aqua Regia* is very unstable and oxidises very rapidly. It cannot be stored for long periods of time and only the volume needed for each set of experiments was prepared every time. Although the CISED method is simple to carry out, the chemometric processing of data required specialised software, CISED developed by MATLAB, which was provided by BGS.

Since it was expected that concentrations of major and minor elements would be compared to soils and other sediments (Cave *et al.*, 2004; Cave and Wragg, 1997), each filtrate had to be duplicated at a lower concentration. A small amount of filtrate (1 ml) was transferred to a sterile universal vial and 9 ml of respective extractant was added to the universal vial to make up the 10 ml of diluted sample. All the extracts were then analysed by ICP-MS for Al, Ba, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr, Ti, V and Zn. These elements are the main PHEs and major elements in soils and sediments that are used for determining associations (Wragg and Cave, 2009b).

4.10 STATISTICAL ANALYSIS

Statistical analysis for the XRF, ICP, IC, pH and Redox data was carried out using the GraphPad Prism software (version 5.0). The replicates for each analysis were imported into the software and the data was first tested for normality using the D'agostini and Pearson Omnibus Normality Test. The values (in this case, the elements) followed a normal distribution and thus were not log transformed (Manly, 1994). Correlation coefficients were carried out for the values between elements, sample points and sites.

4.10.1 Precision

Precision in results was also tested using analysis of coefficient of variance. The mean ($\bar{x}$) and standard deviations (σ) of the replicates were calculated and the coefficient of variation determined using the following equation:

$$Cv = \frac{\sigma}{\bar{x}} x\ 100$$

Equation 2: Coefficient of Variation.

Where: C_v is the coefficient of variation; σ is the standard variation; $\bar{x}$ is the mean.

4.10.2 Errors

Different errors can occur at different stages during experimentation and thus can shift precision and accuracy. Errors have been minimised where possible and taken into consideration at every step of experiments. Parallax errors, when taking pH and Redox measurements, have been reduced by using a thin ruler as thicker rulers can create parallax errors and measurements were taken perpendicular to the ruler. Systematic error was reduced by doing replicates for each sample site (10 boxes) and replicates of replicates within each box (5 cores for XRF, 5 measurements for pH and Redox, 3 cores for ICP, 3 cores for IC).

Systematic errors were also reduced by using different methods to test for the same hypothesis. All instrumentation used during the analytical process was calibrated before each analysis, for example the pH and Redox meter, ICP, IC and XRF. Distribution of pH, Redox, organic loss on ignition data and elemental concentration in sediment (XRF) and pore water (ICP) were illustrated using box and whisker plots, as shown in Figure 15, while ionic content of the pore water and particle size distribution was illustrated using bar charts.

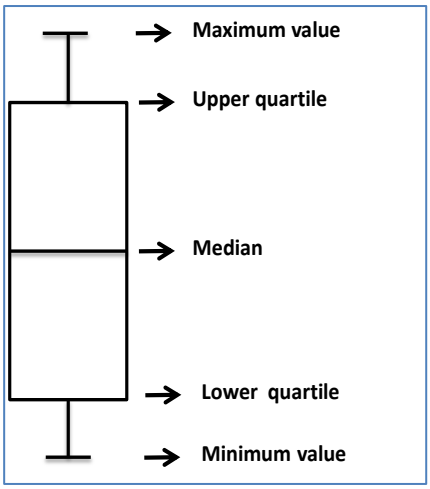


Figure 15: Statistical representation of data using box and whisker plots.

RESULTS
CHAPTER 5

"The beginning of wisdom is found in doubting; by doubting we come to the question, and by seeking we may come upon the truth." – Pierre Abelar.

CHAPTER 5

RESULTS

Chapter 5 presents results from the analyses used for the characterisation of the dredged canal sediments. The electrochemical analyses for pH and Redox are presented first followed by sequential extraction results, which show the component and PHE association for one sample at Belper Bridge with the graphs and bar charts showing the individual components. The results for the rest of the samples from Belper Bridge, Titford and Horseley Fields have been collated and presented in two tables, one for components association and the other one for partitioning of PHEs between the six components. After the sequential extraction results, total concentration of PHEs and major elements analysed by XRF and elemental and anionic concentration using ICP and IC are presented. The results for the organic phase show the organic loss on ignition results and the PAH analysis using GC-MS. Results for particle size, XRD and SEM-EDX are also presented before the chapter concludes with the statistical analysis of data from the various analyses used, for example, particle size vs XRF data.

5.1 PH AND REDOX

5.1.1 Belper Bridge

Figure 16 shows the pH and Redox for the Belper Bridge site. The sediments remained very anoxic in the sediment tanks, even though the sediments had recently been dredged and hence possibly mixed with atmospheric oxygen in the process. The Redox potential (represented by the red plot) from the bottom of the tanks to the top remained negative with a mean Redox potential of -380.0 mV (with a range of -418.0 mV to -317.0 mV at the bottom) and gradually increasing to around -208.0 mV (with a range of -306.0 mV to -160.0 mV for the top 2.0 cm). It should be noted that the Redox potential at the surface was between 0.0 mV and -100.0 mV. Although the sediments in the tank were in contact with oxygen, only a very thin layer of about 0.3 cm was actually oxidised, distinguishable by a reddish grey/brown coloration. Raw data are presented in Appendix 1.1. The pH values were less variable across the sample points ranging between 7.4 to 7.7 for maximum values and 6.7 to 6.8 for minimum values. The median values ranged from 7.1 to 7.2.

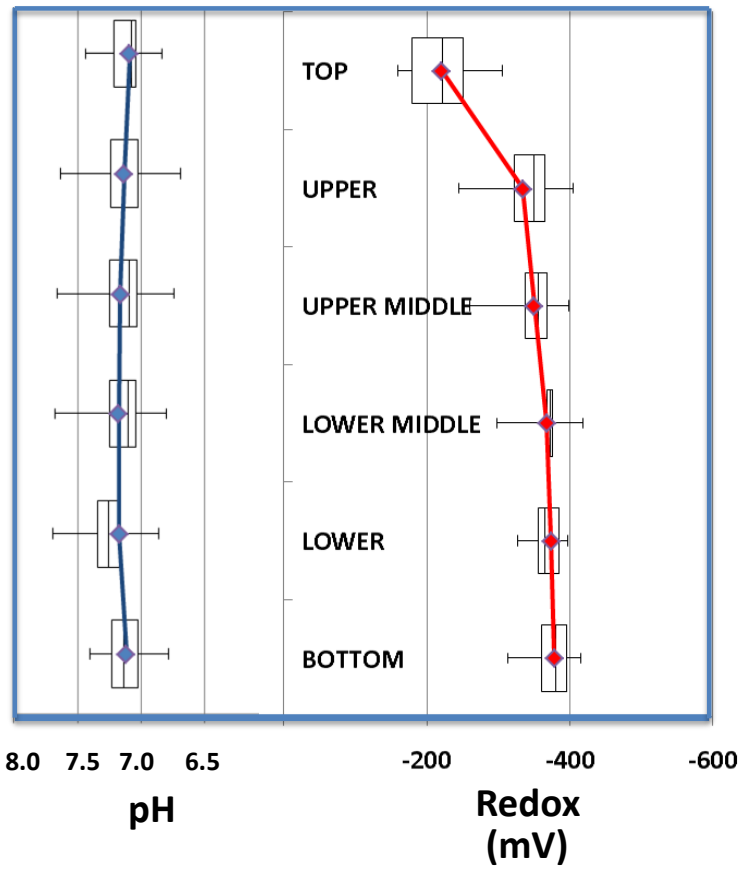


Figure 16: pH and Redox (mV) mean profile for Belper Bridge with box and whisker distribution plots.

5.1.2 Titford

The sediments remained anoxic in the sediment tanks (Figure 17), even though the sediments were in contact with atmospheric oxygen during the dredging process. The Redox potential at the bottom of the tanks remained negative with a mean Redox potential of -258.0 mV (with a range of from -348.0 mV to -148.0 mV) and stayed relatively constant throughout the tank depth before sharply declining to -182.0 mV in the top sample point (with a range of -248.0 mV to -105.0 mV). The sediments in the tank that were in contact with oxygen developed a very fine film, reddish grey/brown in colour, at the surface. Figure 17 shows the sediment tanks for Titford were quite uniform in terms of pH readings which remained in the narrow range of 7.0-7.5. Redox potential although very anoxic was higher than at Belper Bridge. Half of the tanks had values between -350.0 mV to -300.0 mV for the bottom sample point, whereas the other five tanks ranged from -200.0 mV to -148.0 mV for the same sample point. Hence, the distribution was platykurtic and skewed in some cases.

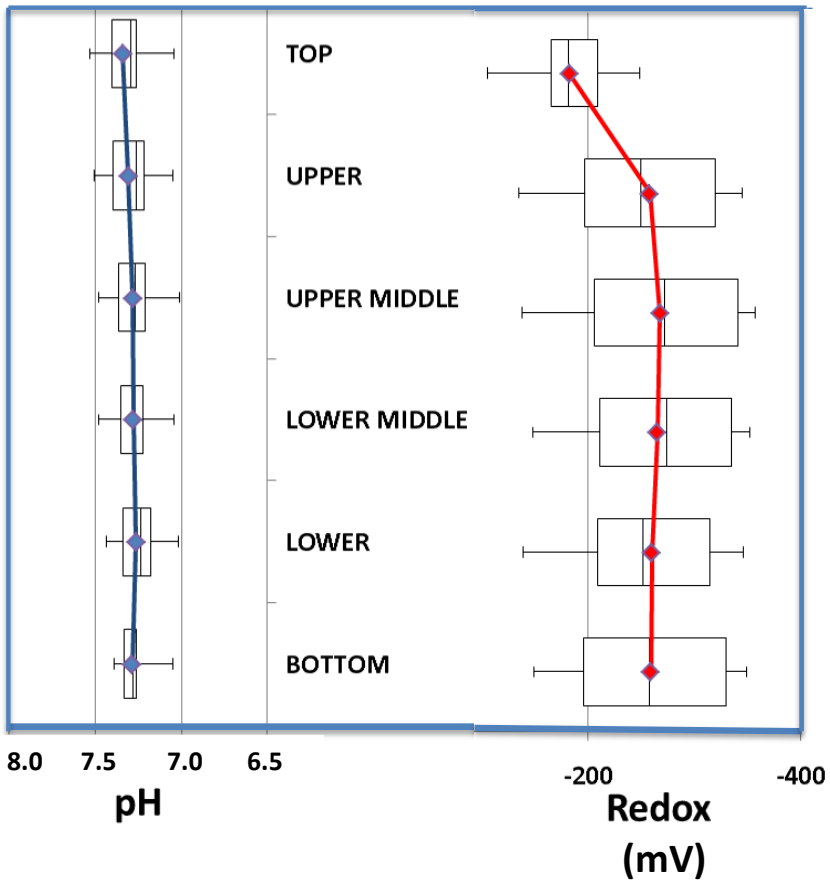


Figure 17: pH and Redox (mV) mean profile for Titford with box and whisker distribution plots.

5.1.3 Horseley Fields Bridge

The mean values for the Redox potential gradually decreased from -375.0 at the bottom of the tanks to -229.0 mV towards the top of the tanks (Figure 18). The mean pH remained at 7.2 to 7.4 throughout the profile for all the tanks. The pH values for the ten tanks ranged from 7.0 to 7.3 for the bottom sample point and from 7.2 to 7.4 for the top sample point. Overall, the pH values for the ten tanks had very little variance. The Redox values on the other hand were different from the first two sites. The Redox potential ranged from -304.0 mV to -417.0 mV for the bottom sample point and from -178.0 mV to -244.0 mV for the top sample point. One of the ten boxes for Horseley Fields Bridge had higher Redox values, ranging from -417.0 mV for the bottom sample point to -318.0 mV for the top sample point is also represented in the box and whisker plot diagram and hence why the median and the mean values are not overlapping.

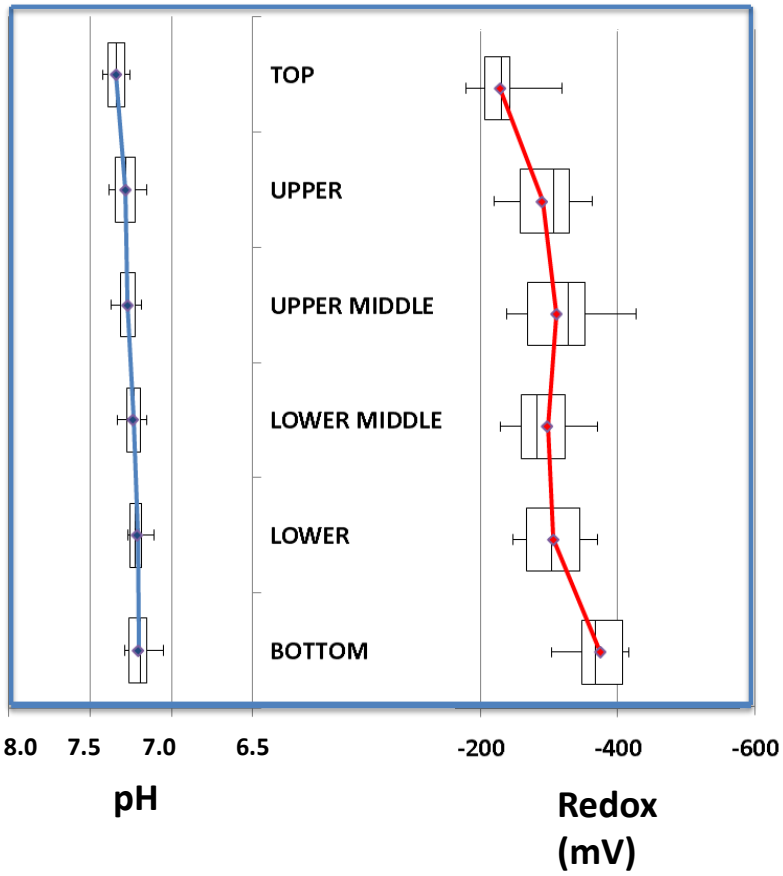


Figure 18: pH and Redox (mV) mean profile for Horseley Fields Bridge with box and whisker distribution plot.

5.2 SEQUENTIAL EXTRACTION

5.2.1 Horseley Fields Bridge

Figure 19 shows the 14 extracts (2x DI, 2x 0.01M, 2x 0.05M, 2x 0.1M, 2x 0.5M, 2x 1M and 2x 5M) during the sequential extraction procedure. The different elements released at the different concentrations of *Aqua Regia* were plotted in the bar charts by the CISED software and also show at which point the elements were released as outlined in Section 4.9.1.

The 14 extractants are plotted against total extractable solids along with the elements released, demonstrated by the bar charts in Figure 19. The CISED software computes the graphs in the order of increasing molarity of *Aqua Regia*. Thus, the more soluble component is shown in Number 1 (Figure 19) and the more stable elements which require higher molarity of *Aqua Regia* are shown in Number 6 (Figure 19).

Once the data were compiled, the CISED software also computed the main six components (different for each sample, depending on the major elements released) in the sediments, derived from the BGS database, data from the experiments and algorithms within the software.

The peaks from the various graphs are used to derive major associations of PHEs in the sediments with the conventional Tessier's fractions. Using the BGS method is more accurate though for canal sediments, as it derives associations that are not necessarily one of the five Tessier's fractions. The fractions are determined using the various peaks, for example, iron and manganese oxides will have high peaks towards the end of the extraction due to the high concentration of Aqua Regia needed to dissolve such components. Similarly, carbonates will have specific peaks at specific extraction stages. Organic components and exchangeable fractions are also shown by peaks at particular stages, for example, when hydrogen peroxide is added, or with specific elements being released in the case of exchangeable fractions.

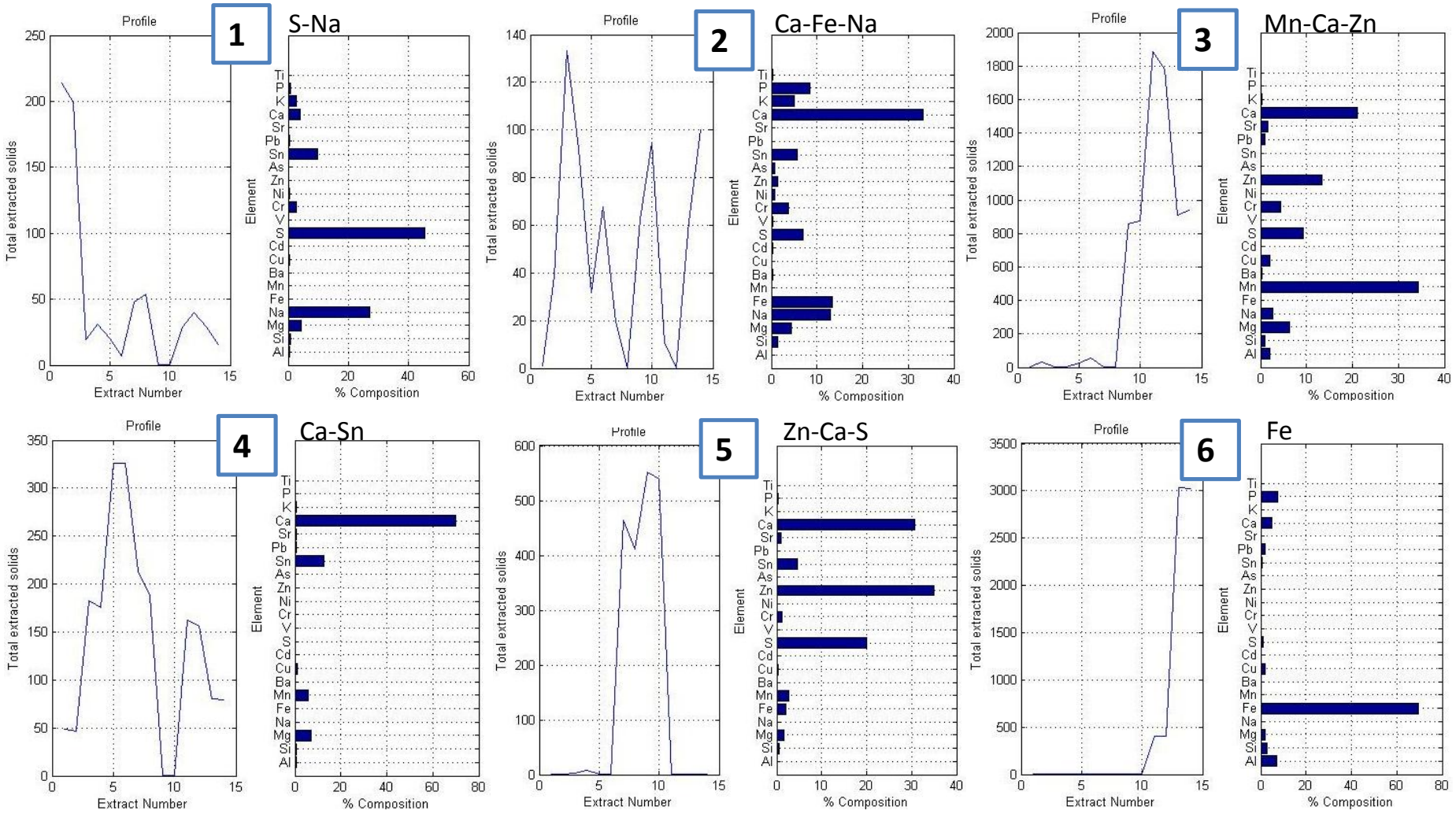


Figure 19: Sequential extraction profiles computed by the MATLAB software showing the six components (above bar charts) and where the elements associated with the components are released- concentration in mg/kg for the total extractable solids.

5.2.2 Components

Component 1 was the S-Na component which related to the soluble PHEs in the pore water. It was composed predominantly of S and Na which are likely to be derived from pore-water salts in the sediments. Component 2 has been identified as the exchangeable or organic phases (please refer to Section 7.7.1 for discussion on identification of the different components). Component 3 could be a carbonate due to the high concentration of calcium released. Component 4 has been identified as a zinc-calcium-sulphur component which could be a zinc sulphate. This component was a recurring component in all the samples and was typical to these anoxic canal sediments. Component 5 was identified as a manganese oxide or a mixed manganese-zinc-calcium oxide. Component 6 was identified as an iron oxide phase due to late extraction of the phase.

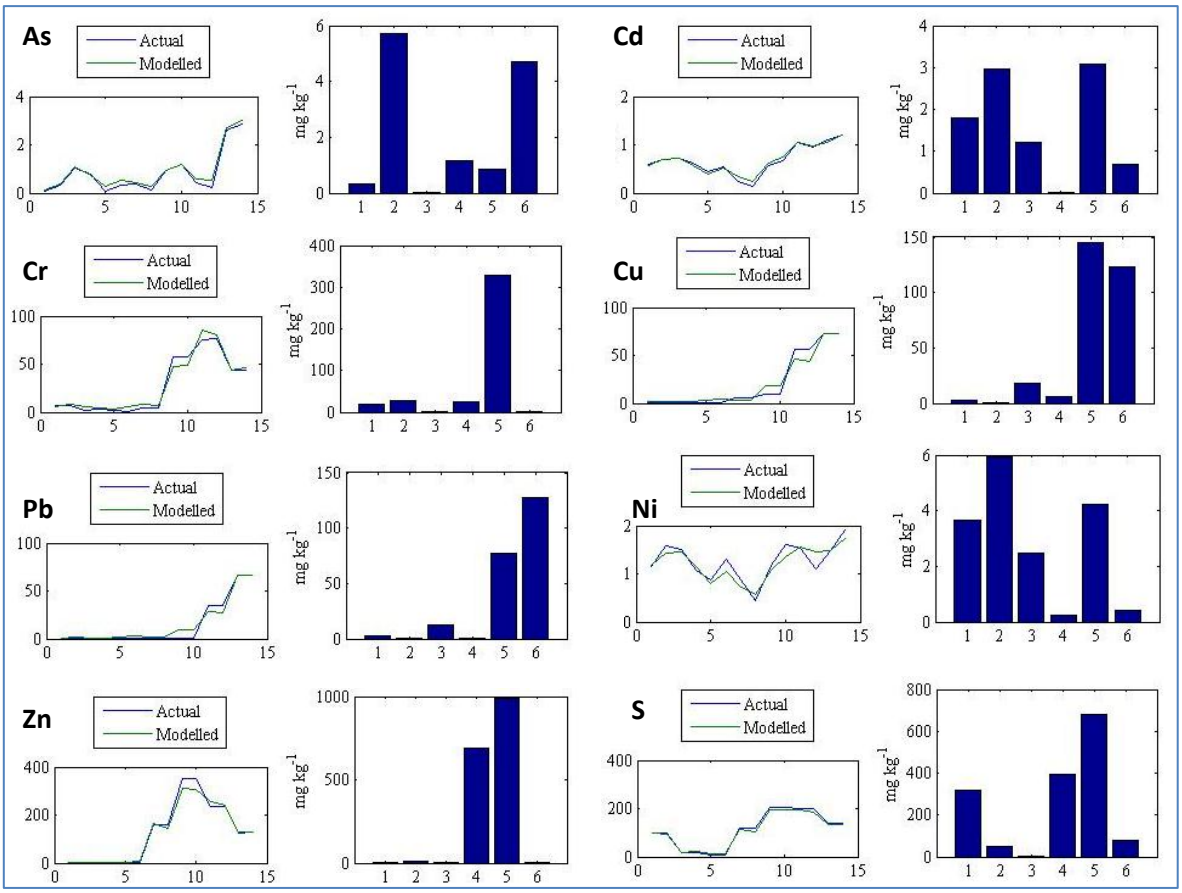


Figure 20: Association of PHEs with the 6 components. Bar charts show the extractable solids in mg/kg and plots show at what stage in the sequential extraction the PHEs were released.

5.2.3 PHE association

The PHEs were associated with one or more of the components (discussed in Section 5.2.2) at different percentages. The concentrations of the PHEs associated with the six components are

shown in Figure 20, for example, arsenic was associated mainly with component 2 and 6 and to a lesser extent, components 1, 4 and 5. Once the components have been identified, the corresponding fractions according to conventional extraction methods can be assigned. For example, component 6 (Figure 20) was a Fe oxide phase and component 2 was identified as an organics/exchangeable phase. Thus, it can be deduced that As in the given sample was mainly associated with these two phases. Other PHEs, on the other hand, were associated mainly with either the soluble phases or the more stable phases such as the iron oxides. The line graphs for each elements show the modelled and actual extraction points for each PHE.

5.2.4 Samples from Belper Bridge, Titford and Horseley Fields Bridge and their corresponding components

The sequential extraction procedure was repeated in duplicate for the rest of the samples. Table 10 shows the results for the samples from Horseley Fields, Belper Bridge and Titford for the top, middle and bottom sample points. The six components are shown on the first line followed by the different assessments of the associations of each component. The components are mainly iron oxides, manganese oxides, sulphates/sulphides, exchangeable, organic, carbonate and soluble. S-Na is the main component indicating soluble phases, Fe and Mn indicate iron and manganese oxides, Ca indicate carbonate, Mg and K for exchangeable and S for sulphate/sulphide. Zinc is peculiarly part of many of the components in all samples and indicates that it may be involved with the chemical behaviour of the sediments. Table 11 shows the different components and the relative elemental associations. The stronger associations were assigned the highest value of 4, and the lower the association (< 10%), the lowest value of 1. The elements can be strongly and equally associated with two or more components and thus the relative association is divided among the different components. Thus, the total concentration of element extracted from the sediments is equally divided, depending on the ratio of its associations with the different components. Since canal sediments are anoxic and have not been catalogued by BGS, some of the associations are unidentified (U). Most of the unidentified associations were components made up of Zn, P or S which indicates either a phosphate or zinc sulphide. Zinc is present in all the samples as a separate component in the sediments and this feature has not been widely documented in the literature and also due to the fact that the sequential extraction method has not previously been used with canal sediments. Most of the other associations were similar to conventional soils fractions and other sediments, for example, the exchangeable, organic, iron and manganese oxides and carbonates.

Table 10: Components for the other samples for Belper Bridge, Titford and Horseley Fields Bridge, with their corresponding fractions

	Belper Top	Belper Middle	Belper Bottom	Titford Top	Titford Middle	Titford Bottom	Horseley F. Top	Horseley F. Middle	Horseley F. Bottom
component	Ca-S-Zn	S-Na-Ca	S-Na	S-Na-K	S-Na	S-Na-Ca	S-Na	S-Ca-Na	S-Na-Fe
Fraction	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
component	K-Zn-P-Ca	Ca-Na	S-Zn-Mg	Na	Ca-Na	Ca-Na	Zn-Ca	Mn-Sn	Zn-Ca-S
Fraction	Organic	Carbonate	Sulphate	Soluble	Carbonate	Carbonate	Carbonate	Manganese Oxide	Sulphate
component	Na-S-K	Mg-K	Fe-Ca-Mg	Ca	Fe-Ca-P	Ca-Fe	Mn-Fe-Zn	Zn-S-Mn	Fe-P-Mn
Fraction	Soluble	Exchangeable	Carbonate Exchangeable	Organic Carbonate	Organic	Organic	Iron Oxide Manganese Oxide	Sulphate Manganese Oxide	Iron Oxide Manganese Oxide
component	Ca-P-Zn	Ca-Na	K-Na-P	Ca-S-Zn-Fe	Zn-Si-S	P-Mg-Na	Ca-Ba-Mg-Mn	Ca-Mg	Mn-Zn-Fe-S
Fraction	Carbonate	Carbonate	Organic	Iron Oxide Manganese Oxide Sulphate	Sulphate	Unidentified	Carbonate	Carbonate Exchangeable Organic	Iron Oxide Manganese Oxide Sulphate
component	Ca-Na	Ca-P-Fe	Na-Ca	Zn-Ca-P	Ca-P-Fe-Al-Zn	Ca-Zn-S	Ca-S	Fe-Mn	Ca-Fe-Mn
Fraction	Carbonate	Iron Oxide	Carbonate	Iron Oxide Manganese Oxide Sulphate	Unidentified	Sulphate Carbonate	Sulphate	Iron Oxide Manganese Oxide	Iron Oxide Manganese Oxide Carbonate
component	Fe-P	Fe-P-Ca	Fe-P-Ca	Fe-P	P-Fe	Fe-P	Fe-Ca-P	Fe-Ca	Ca
Fraction	Iron Oxide	Iron Oxide	Iron Oxide	Iron Oxide	Iron Oxide	Iron Oxide	Iron Oxide	Iron Oxide	Carbonate

Table 11: Samples from 3 sites, elemental distribution (soluble/ pore-water (W), carbonate (C), exchangeable (E), organic (O), iron oxide (F), manganese oxide (M), sulphate (S) and unidentified (U)). Strong association assigned a value of 4 and weak association a value of 1

H5T										T7T										B9T									
COMP	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As	**COMP**	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As	**COMP**	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As
1	**S**	1	1	1	2	1	2	1	3	**1**	**W**	4	1	4	1	1	1	2	1	**1**	**W**	4	1	2	1	1	1	2	1
2	**C**	2	4	3	1	2	1	2	2	**2**	**U**	1	1	3	1	1	2	1	1	**2**	**S**	1	4	3	1	2	1	4	1
3	**FM**	3	4	2	4	4	4	1	1	**3**	**OC**	1	1	4	1	1	2	1	2	**3**	**W**	1	1	3	1	1	2	2	1
4	**W**	4	1	4	2	1	1	4	1	**4**	**FM**	4	2	2	1	1	1	1	1	**4**	**O**	1	3	3	4	4	4	2	3
5	**F**	2	1	2	4	3	1	1	3	**5**	**FMS**	2	4	4	2	4	1	4	1	**5**	**F**	2	1	3	2	2	3	2	4
6	**C**	2	1	4	1	1	2	4	4	**6**	**F**	2	2	3	4	4	4	1	4	**6**	**C**	1	1	4	1	1	3	3	3
H5M										**T7M**										**B9M**									
COMP	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As	**COMP**	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As	**COMP**	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As
1	**W**	3	1	3	1	1	1	4	2	**1**	**W**	4	1	4	1	1	2	2	1	**1**	**W**	4	1	3	1	1	2	1	1
2	**CEO**	1	2	2	1	1	1	4	4	**2**	**C**	1	1	4	1	1	2	2	2	**2**	**C**	1	1	4	1	1	2	2	2
3	**S/M**	4	4	4	1	2	3	1	1	**3**	**O**	3	2	1	1	1	1	1	1	**3**	**E**	1	1	3	1	1	1	4	1
4	**M**	2	2	1	2	2	4	1	1	**4**	**S**	3	4	4	1	2	1	4	1	**4**	**C**	2	4	3	1	2	1	1	1
5	**FM**	2	2	2	4	4	3	2	3	**5**	**U**	1	4	1	4	4	4	2	2	**5**	**F**	3	4	4	4	4	1	4	1
6	**F**	2	1	2	2	2	1	2	1	**6**	**F**	2	1	4	4	2	3	1	4	**6**	**F**	2	1	3	3	2	4	1	4
H5B										**T7B**										**B9B**									
COMP	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As	**COMP**	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As	**COMP**	**FR:**	S	Zn	Ni	Pb	Cu	Cr	Cd	As
1	**W**	3	1	3	1	1	1	4	1	**1**	**W**	4	1	2	1	1	1	1	3	**1**	**W**	4	1	3	1	1	3	3	2
2	**S**	4	3	4	1	1	1	2	3	**2**	**C**	1	1	2	1	1	1	1	3	**2**	**CE**	1	1	3	1	1	2	1	3
3	**C**	1	2	2	1	1	1	2	3	**3**	**O**	1	1	4	1	1	4	1	1	**3**	**S**	4	4	1	1	1	1	3	1
4	**FMS**	4	4	4	2	4	4	1	1	**4**	**U**	1	1	1	1	1	1	4	2	**4**	**O**	2	1	1	1	1	1	4	1
5	**FMC**	1	1	3	1	1	1	3	4	**5**	**SC**	4	4	1	1	1	1	1	1	**5**	**C**	1	1	4	1	1	3	3	2
6	**FM**	1	1	1	4	4	2	1	3	**6**	**F**	1	1	2	4	4	3	1	4	**6**	**F**	1	1	2	4	4	4	3	4

5.3 ELEMENTAL CONCENTRATION IN SEDIMENT

5.3.1 Main PHEs under investigation

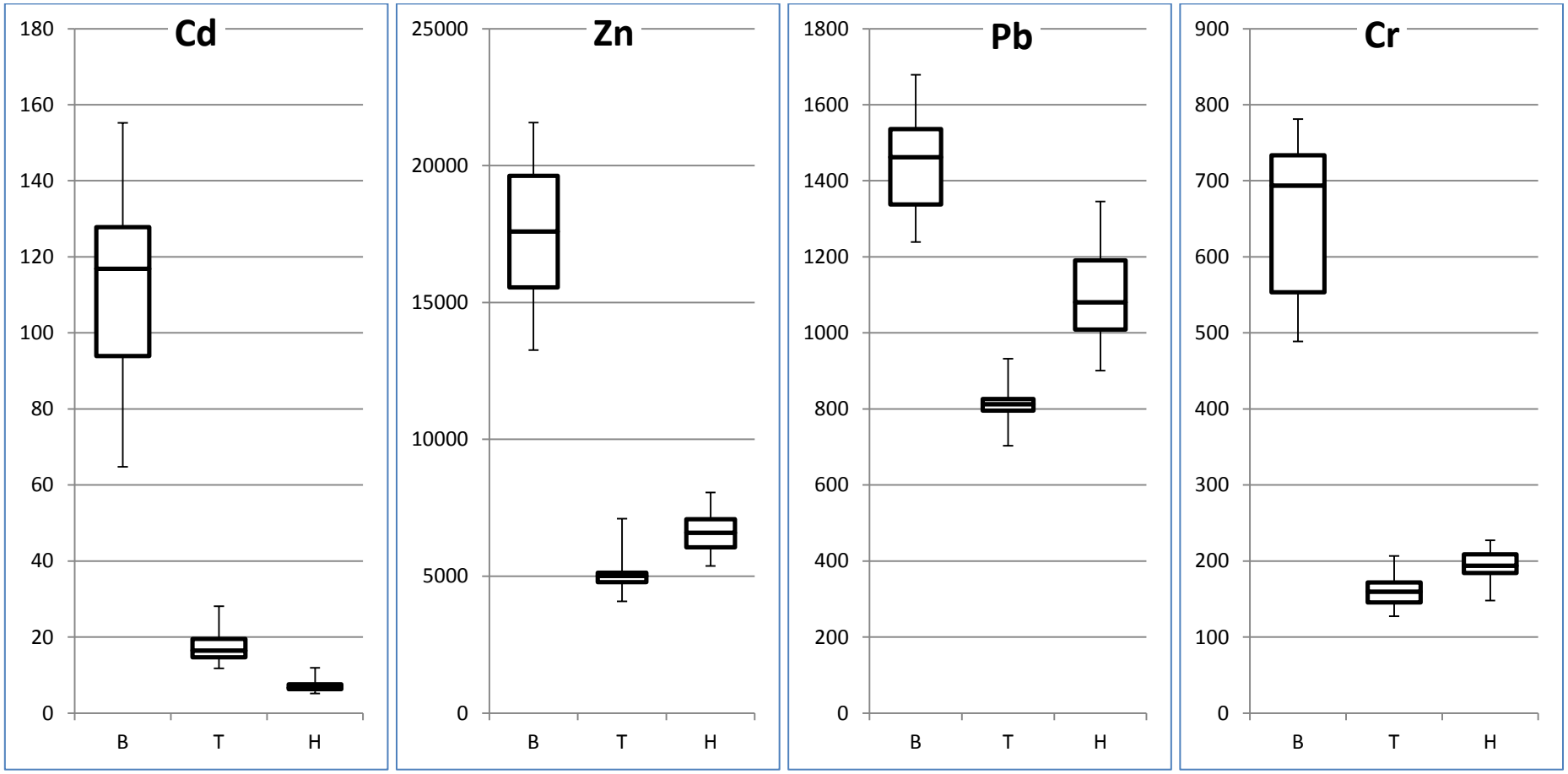


Figure 21: Cd, Zn, Pb and Cr concentrations in sediments for Belper Bridge (B), Titford (T) and Horseley Fields Bridge (H). Concentrations in mg/kg.

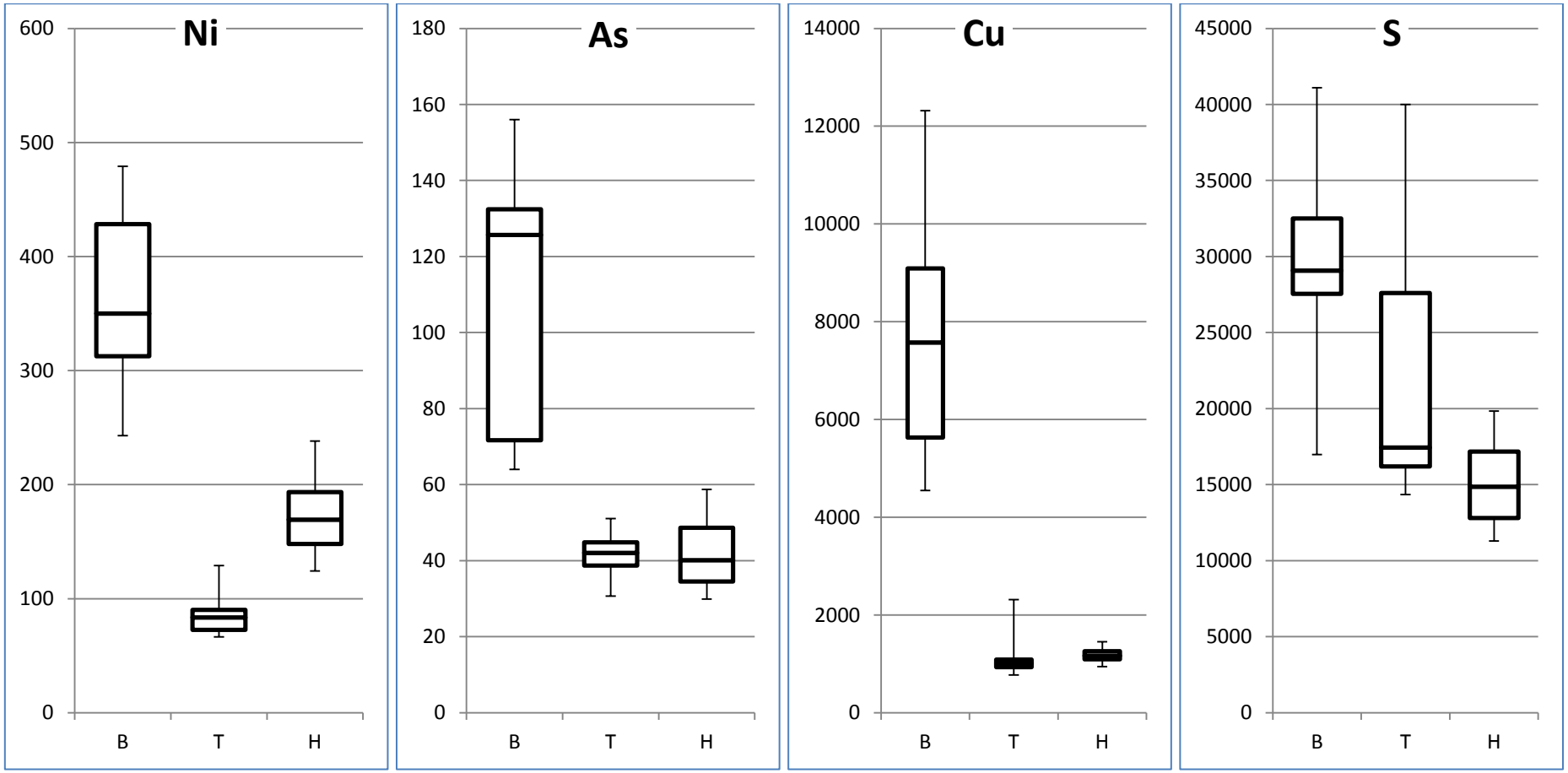


Figure 22: Ni, As, Cu and S concentrations in sediments for Belper Bridge (B), Titford (T) and Horseley Fields Bridge (H). Concentrations in mg/kg.

Figure 21 and Figure 22 show the concentrations of the main PHEs in the sediments. The concentrations were determined by XRF and show total concentrations in the canal sediments. Sulphur has been included in the list due to the high concentration of sulphur in the sediments and its significance in canal sediments (as discussed in Chapter 3). Zinc, copper and sulphur are the three elements with highest concentrations. Cadmium, lead, chromium, nickel and arsenic concentrations are all below 2000.0 mg/kg. All PHEs have higher concentration at Belper Bridge compared to the other two sites. Cadmium is the only PHE with higher concentration at Titford compared to Horseley Fields Bridge. The other PHEs show higher (or similar) concentrations at Horseley Fields Bridge compared to Titford. Sulphur is the only element where concentrations decline from Belper Bridge to Titford and to Horseley Fields Bridge.

5.3.2 Other PHEs present in sediments

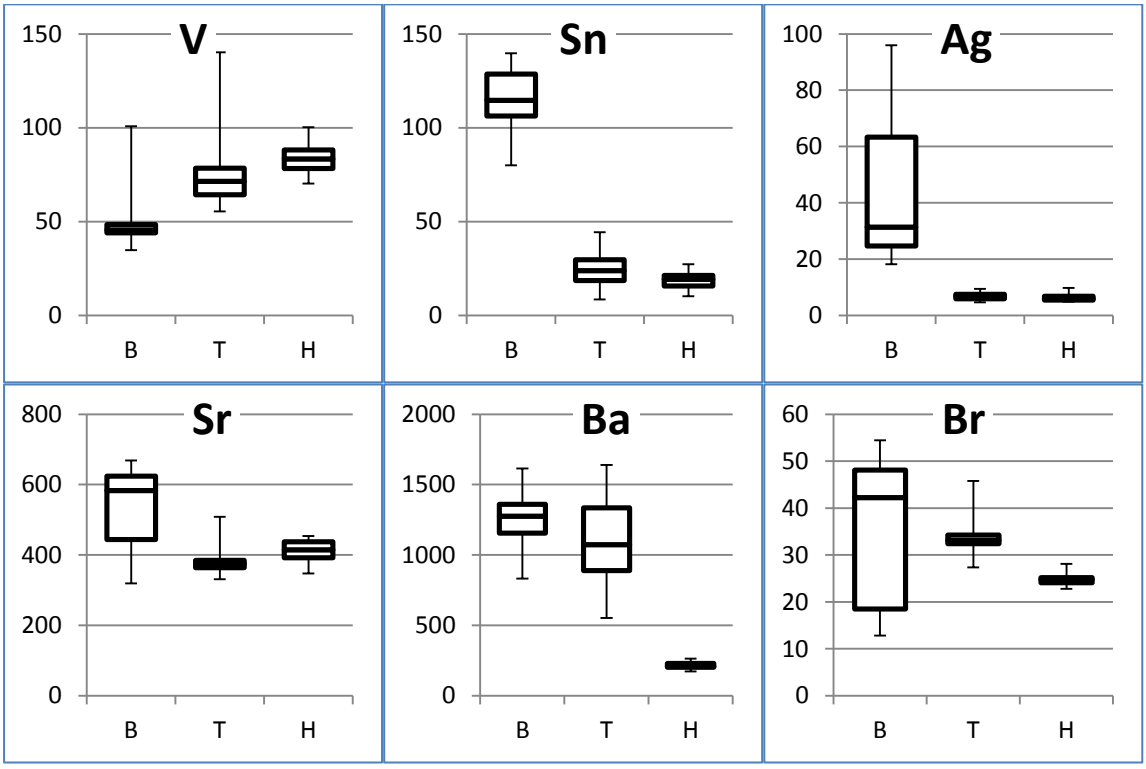


Figure 23: V, Sn, Ag, Sr, Ba and Br concentration in sediments for Belper Bridge (B), Titford (T) and Horseley Fields Bridge (H). Concentrations in mg/kg.

Other PHEs were also present in the sediments and concentrations were determined by XRF (complete set of XRF data can be found in Appendix 1.1). Most of these elements have concentrations below 200.0 mg/kg, except for strontium and barium which have concentrations above 200.0 mg/kg as shown in Figure 23. The distributions of the elements do not follow the

same pattern as the main PHEs (Section 5.3.1), for example, vanadium concentration increases from Belper Bridge to Titford to Horseley Fields Bridge. Strontium and bromium concentrations decreased in order of site.

5.3.3 Major elemental concentrations in sediments

Figure 24 shows the major element concentrations in the sediments. Aluminium, silicon, magnesium and potassium follow the same distribution with higher concentrations of the elements at Titford compared to the other two sites. Phosphorus and sodium follow the same distribution with higher concentration at Belper Bridge followed by Titford and Horseley Fields Bridge.

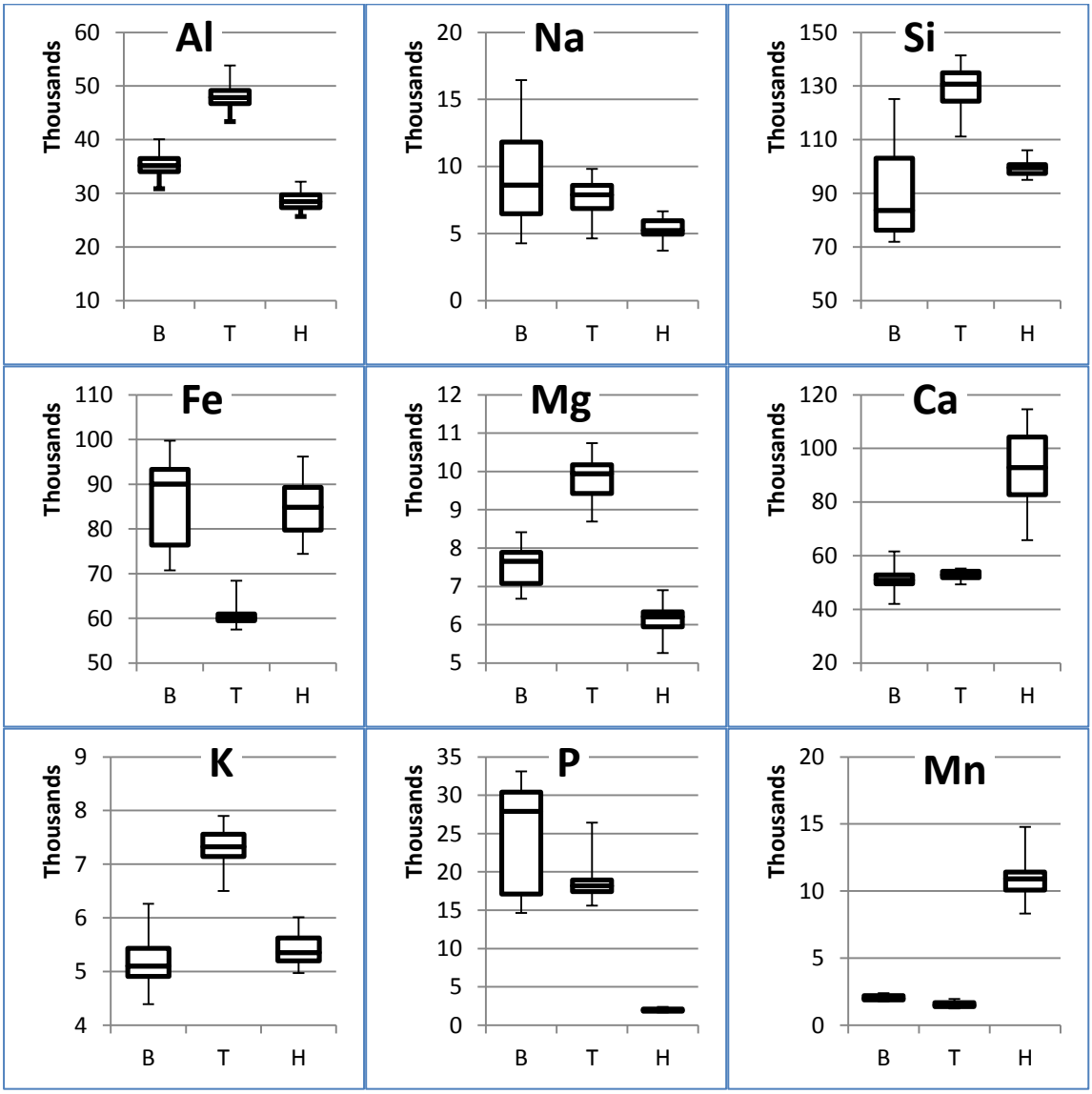


Figure 24: Major elemental concentrations in sediments for Belper Bridge (B), Titford (T) and Horseley Fields Bridge (H). Concentrations in mg/kg.

5.4 ELEMENTAL CONCENTRATION IN PORE WATER

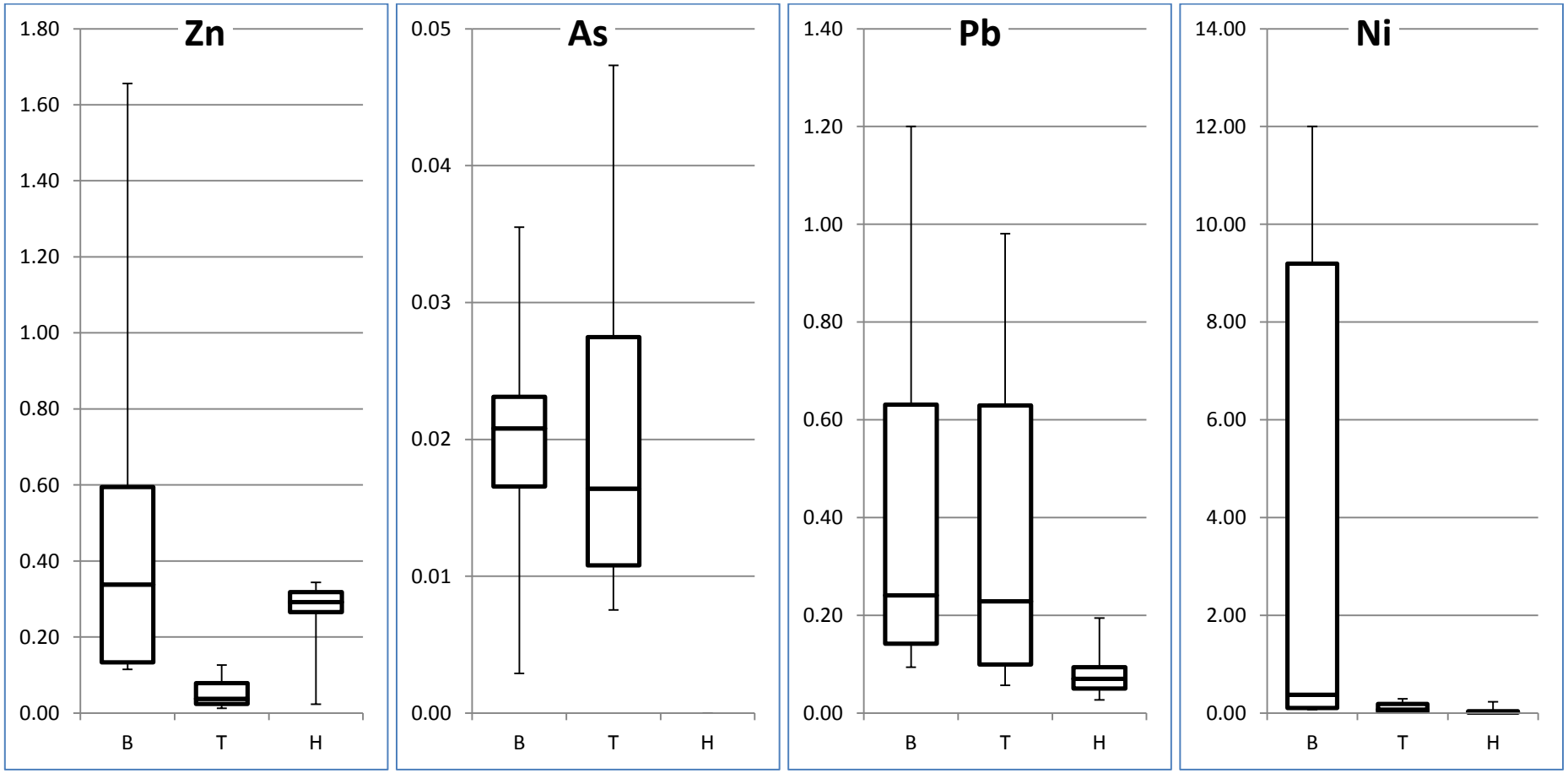


Figure 25: Elemental concentrations in pore water for Belper Bridge (B), Titford (T) and Horseley Fields Bridge (H). Concentrations in mg/l.

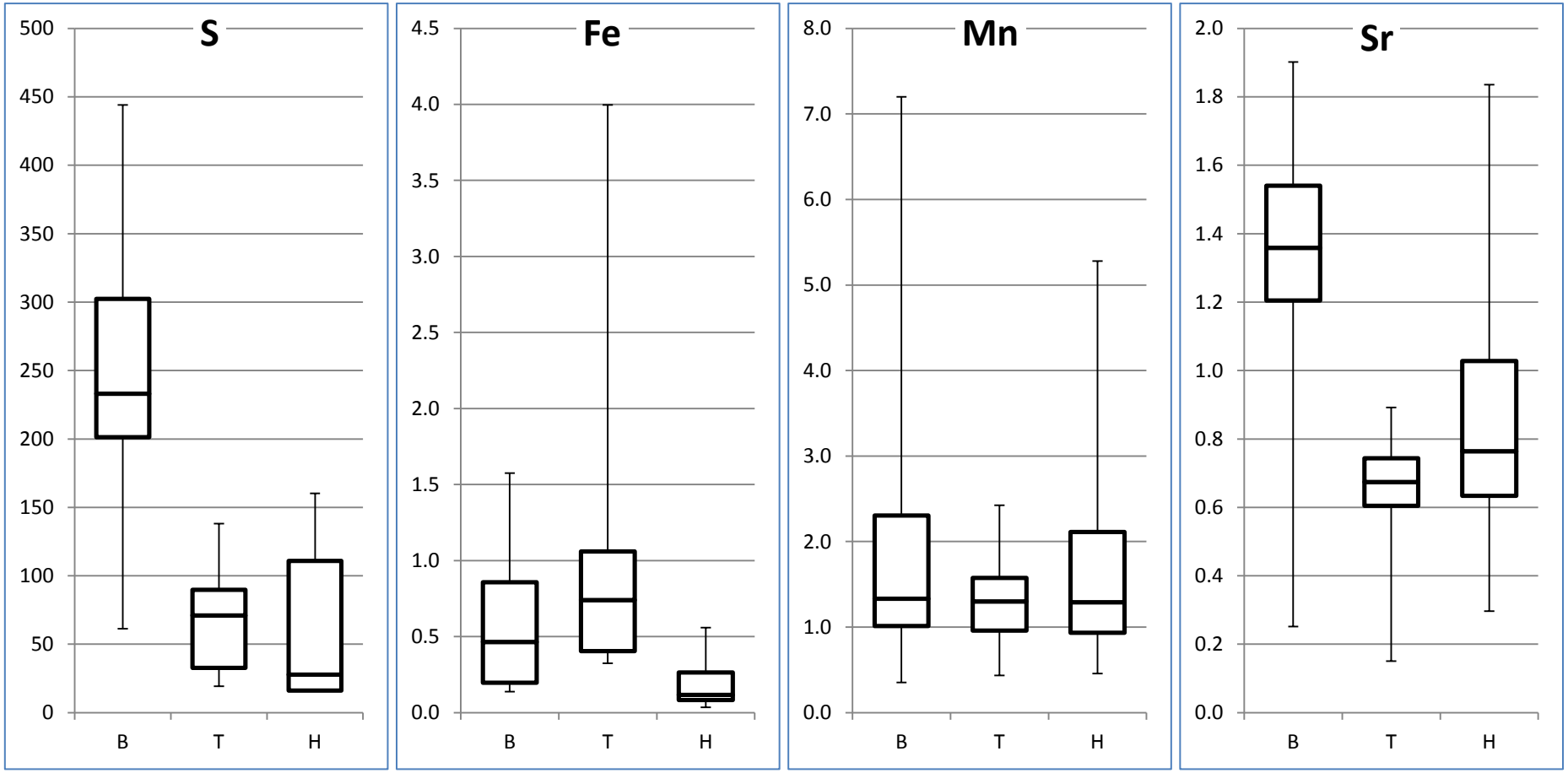


Figure 26: Elemental concentrations for S, Fe, Mn and Sr in pore water for Belper Bridge (B), Titford (T) and Horseley Fields Bridge (H). Concentrations in mg/l.

Figure 25 and Figure 26 show the box and whisker plots for the PHE concentrations in the pore water in the sediments. The PHEs under investigation, such as copper, cadmium and chromium, were below detectable limits and thus are not shown in Figure 25 and Figure 26. The box and whisker plots for the eight elements above are platykurtic, due to the different concentrations between the supernatant and top, middle and bottom sample points. Sulphur, for example, has a higher concentration in the supernatant compared to the bottom sample point with median concentrations of 340.0 mg/l for the supernatant and 163.0 mg/l for the bottom sample point. The other PHEs shown in Figure 25 and Figure 26 follow the same distribution with higher concentrations in the supernatant compared to the pore water in the different sediment sample points (top, middle and bottom).

5.5 ANIONIC CONCENTRATION IN PORE WATER

5.5.1 Belper Bridge

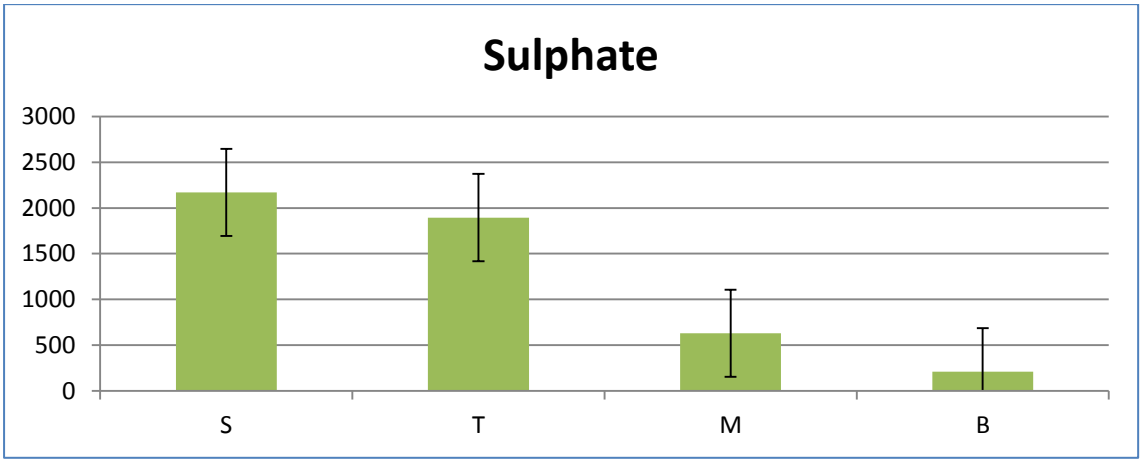


Figure 27: Sulphate concentrations in pore water, Belper Bridge for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Sulphate levels are highest in the supernatant and top sample point of the tanks with a mean of 2170.0 mg/l for the supernatant and 1895.0 mg/l for the top sample point (Figure 27). There is a significant difference for the medium sample point and lower sample points of the tanks with a mean concentration of 631.0 mg/l for the medium sample point and a much lower concentration of 210.0 mg/l for the bottom sample points.

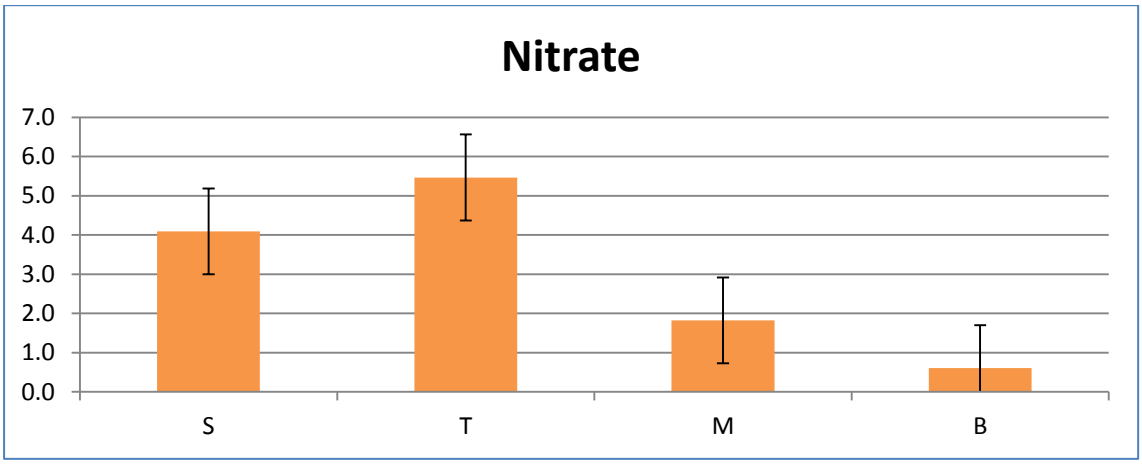


Figure 28: Nitrate concentrations in pore water, Belper Bridge for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Nitrate concentration follows the same pattern with higher concentrations in the upper sample points with a higher mean concentration in the top sample point compared to the supernatant with 5.5 mg/l and 4.1 mg/l respectively (Figure 28). The middle and bottom sample points had lower mean concentrations of 1.8 mg/l and 0.6 mg/l, respectively.

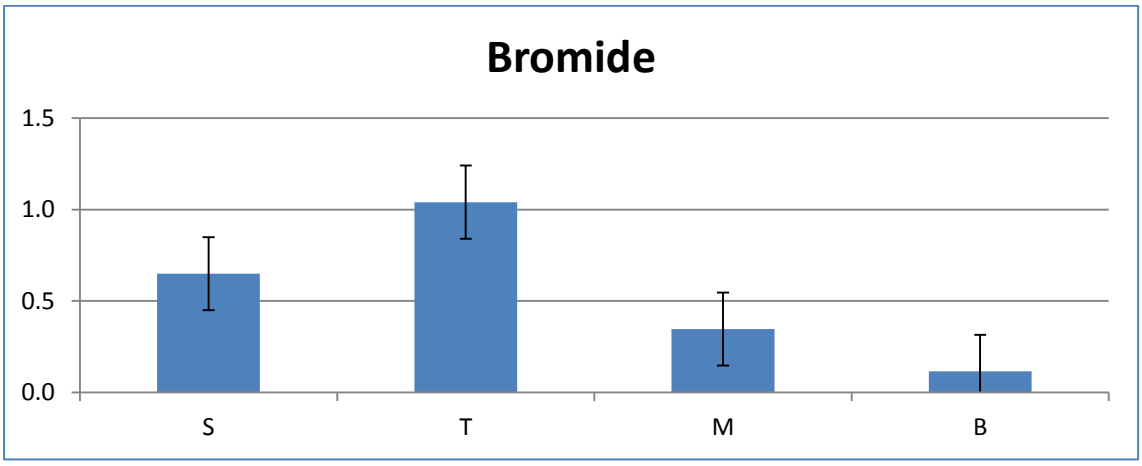


Figure 29: Bromide concentration in pore water, Belper Bridge for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Bromide concentrations follow the trend of nitrates concentration closely, as shown in Figure 29. In fact, statistical analysis on raw data shows that there is a 0.02% chance of randomly observing an effect this large in an experiment of this size. The effect is considered extremely significant with a P value of 0.0002. Bromide concentrations are lower, with supernatant, top and middle sample points at 0.6, 1.0, 0.3 mg/l, respectively.

5.5.2 Titford

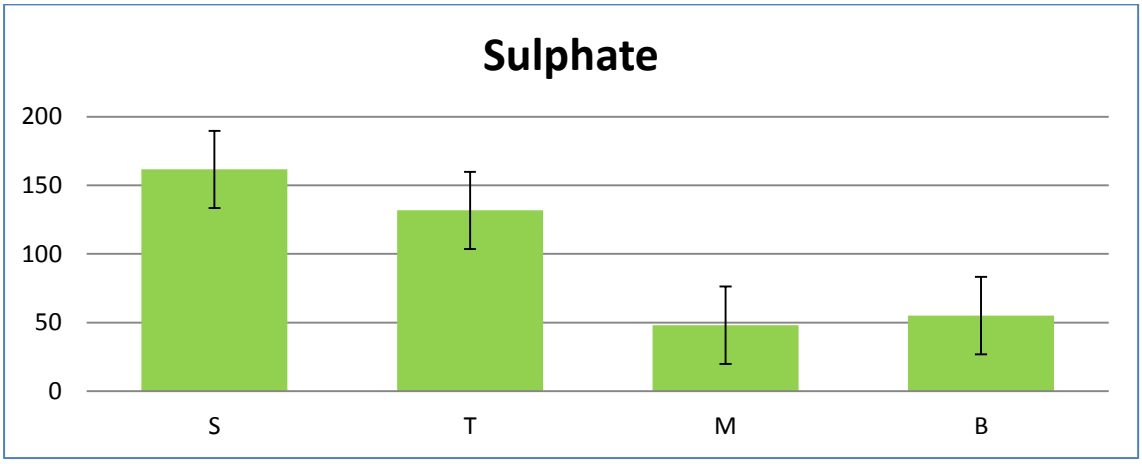


Figure 30: Sulphate concentrations in pore water, Titford for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Sulphate concentrations for Titford follow the same pattern as Belper Bridge (Figure 30) but with lower mean concentrations of 161.0 mg/l for the supernatant, 131.0 mg/l for the top sample point, 48.0 mg/l for the middle sample point and 55.0 mg/l for the bottom sample point, which is slightly higher than the middle sample point.

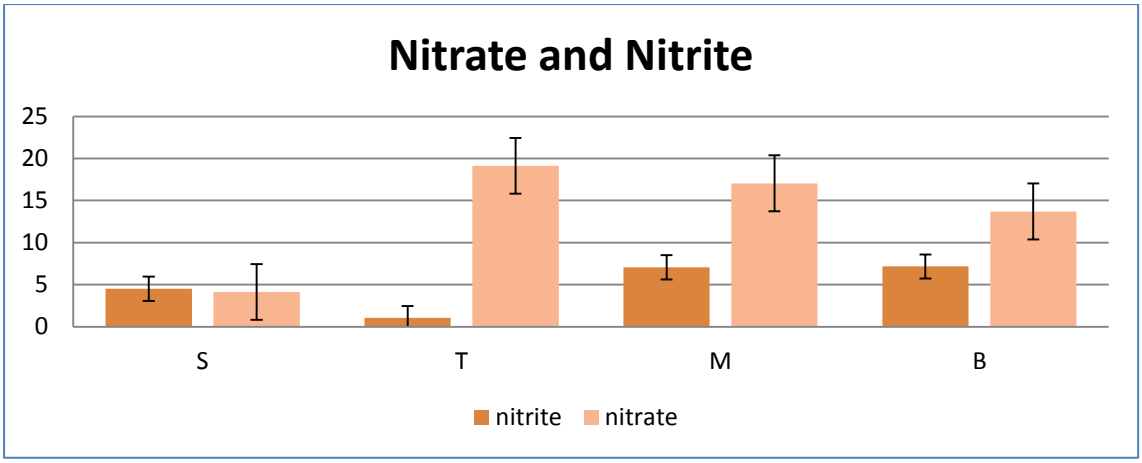


Figure 31: Nitrate and Nitrite concentrations in pore water, Titford for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Nitrate concentrations is lower in the supernatant compared to the sediment sample points (Figure 31) with a concentration of 4.4 mg/l compared to the top, middle and bottom sample points with 19.0, 17.0 and 14.0 mg/l, respectively. This is consistent with the results from Belper Bridge. Nitrite, which was not present at Belper Bridge, follows a different distribution with a higher concentration in the supernatant compared to the top sample point with 4.0 mg/l and 1.0 mg/l, respectively. The middle and bottom sample points have about the same

concentration of nitrites with 7.0 mg/l for the middle sample point and 7.2 mg/l for the bottom sample point.

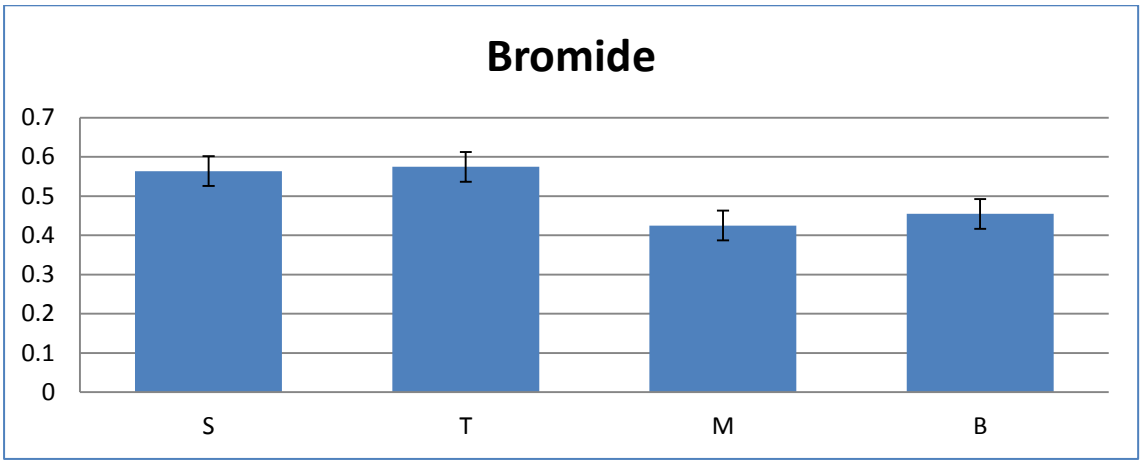


Figure 32: Bromide concentrations in pore water, Titford for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Bromide levels at Titford were the same as Belper Bridge, with 0.5 mg/l for the supernatant and top sample points and 0.4 mg/l for the middle and bottom sample points (Figure 32). Overall, there is a strong correlation between the different ions at Titford with $P < 0.0001$. There is also some correlation between sample points at Titford with $P < 0.001$ for supernatant and top sample points between sulphates and the other ions; nitrates, nitrites and bromides. There is no significant correlation between the other ions.

5.5.3 Horseley Fields Bridge

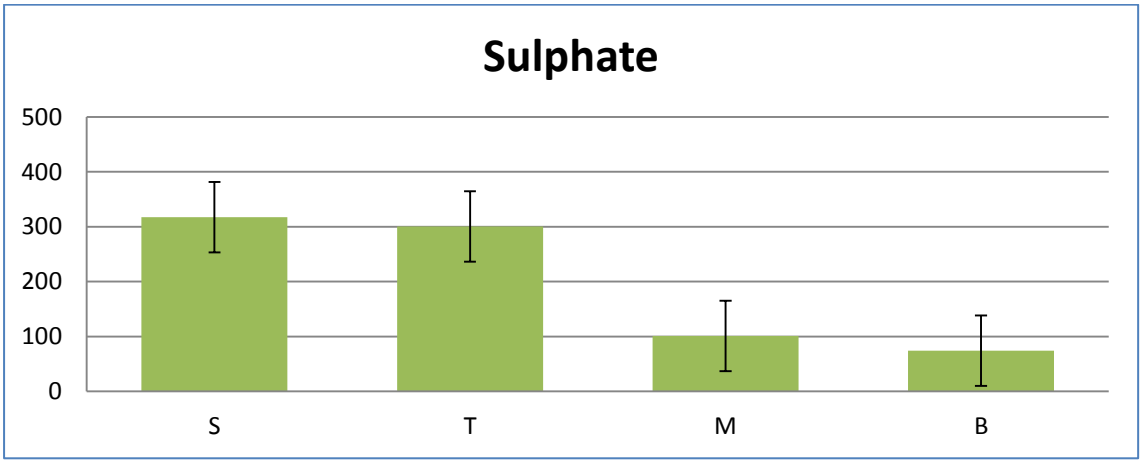


Figure 33: Sulphate concentrations in pore water, Horseley Fields Bridge for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Sulphates at Horseley Fields Bridge follow the same pattern as the other two sites with higher concentration in the supernatant and gradually decreasing with the lowest concentration in the

bottom sample points (Figure 33). The concentrations are higher than Titford but lower than Belper Bridge site, with concentrations starting at 317.0 mg/l for the supernatant, followed by 300.0 mg/l, 100.0 mg/l and 74.0 mg/l for the top, middle and bottom sample points, respectively.

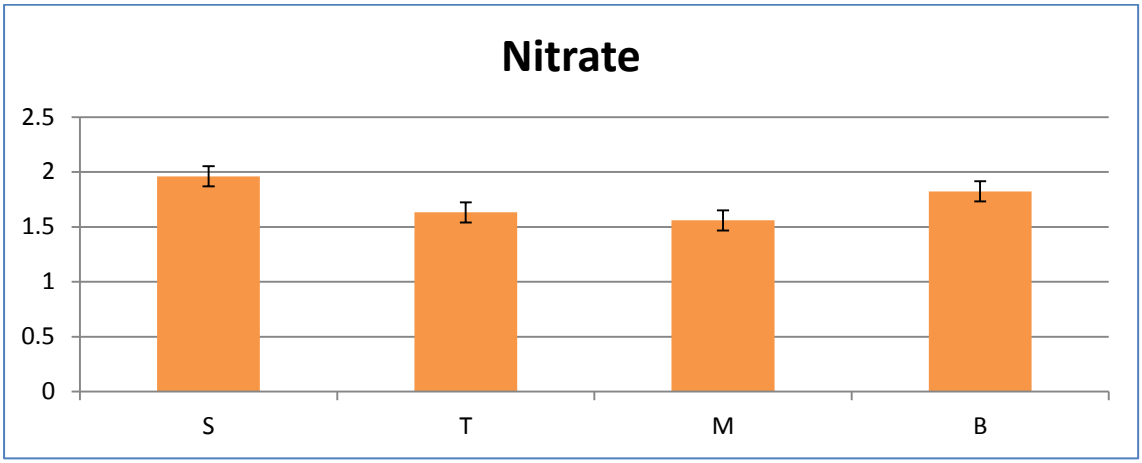


Figure 34: Nitrate concentrations in pore water, Horseley Fields Bridge for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

Nitrates concentrations at Horseley Fields Bridge do not follow the same pattern as Titford and Belper Bridge (Figure 34). The nitrate concentration is higher in the supernatant compared to the concentrations in the sediment sample points. The bottom sample points also have higher concentrations of both nitrates and bromides (Figure 35) at 1.8 and 0.6 mg/l, respectively. The top and middle sample points have the same concentrations of both nitrates and bromides at 1.6 mg/l and 0.4 mg/l, respectively.

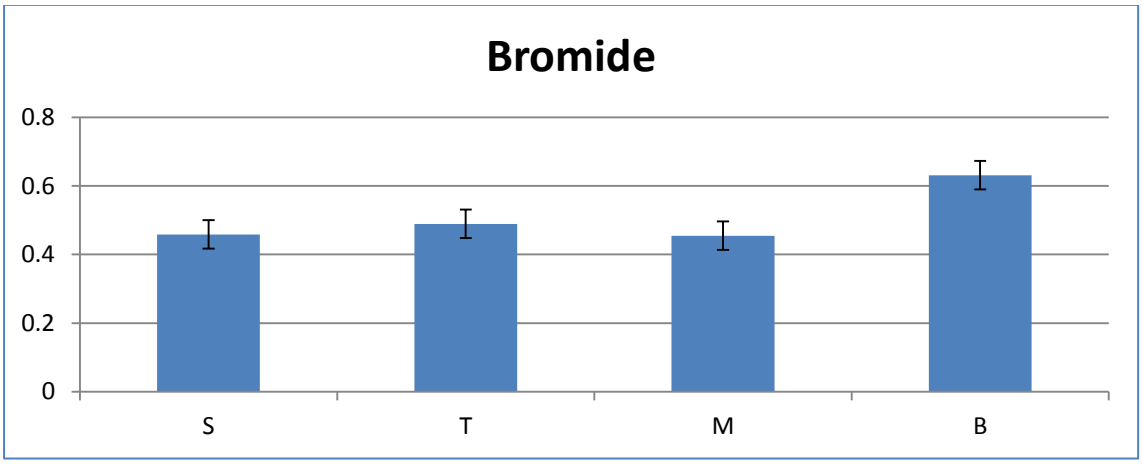


Figure 35: Bromide concentration in pore water, Horseley Fields Bridge for supernatant (S), top (T), middle (M) and bottom (B) samples. Concentrations in mg/l.

5.6 ORGANIC LOSS ON IGNITION

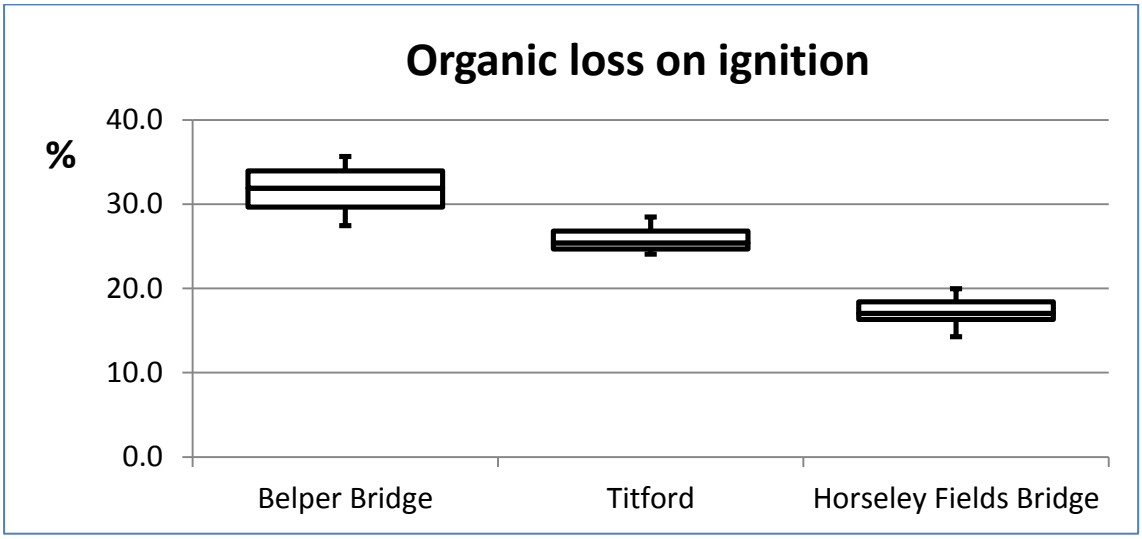


Figure 36: Organic loss on ignition for 3 Belper Bridge, Titford and Horseley Fields Bridge.

5.6.1 Belper Bridge

Results from organic loss on ignition for Belper Bridge (as shown in Figure 36) showed that the organic matter content of the sediments did not vary widely between the sample points. The median values for the three sample points were between 31.0 and 32.0% with maximum values of 35.2 to 36.2% and minimum values of 25.3 to 29.1%.

5.6.2 Titford

Organic matter content in the Titford (as shown in Figure 36) sediments was lower than Belper Bridge with medians ranging from 25.9 to 26.4%. The highest value for organic matter content was in the bottom sample point of the sediments, with 29.9% organic matter content and the lowest was 23.3% for the middle sample point. Titford exhibited similar results as in Belper Bridge, with little variation between the sample points.

5.6.3 Horseley Fields Bridge

Organic matter content at Horseley Fields Bridge was on the other hand different from Titford and Belper Bridge, with median values of 18.0% (Figure 36). The maximum organic matter content for all three sample points was between 19.7% and 20.7%, which is lower than the other two sites. The minimum organic matter content for Horseley Fields Bridge was also lower compared to the other two sites, ranging between 13.0 and 15.0% compared to the other two sites which were both above 20.0%.

5.7 ORGANIC CONTENT- Polycyclic Aromatic Hydrocarbons (PAHs)

Table 12 shows the organic content for the three sites. As it can be seen from the results, all twelve organic compounds found in the samples from the three sites have one of the 17 compounds listed as hazardous. Phenanthrene has the highest concentration with 210.0 mg/kg found at Titford, followed by fluoranthene, present mainly at Belper Bridge and Titford. Most compounds were found in higher concentrations at Belper Bridge and Titford.

Table 12: Organic compounds in sediments, solvents: ethyl acetate and hexane, 3 sites. Concentrations in mg/kg

Compound:	Belper Bridge		Titford		Horseley Fields Bridge	
	Ethyl acetate	Hexane	Ethyl acetate	Hexane	Ethyl acetate	Hexane
Acenaphthene	34.2	33.5	35.6	64.4		4.2
Fluorene	34.1	35.3	27.6	49.5		
Phenanthrene	90.5	92.6	126.4	210.0	5.3	14.7
Anthracene	54.3	55.2	45.3	65.5		5.5
Fluoranthene	111.5	117.6	114.0	193.2	10.1	17.2
Pyrene	114.9	123.2	89.6	154.3	9.5	13.2
Benzo(a)anthracene	34.2	35.5	32.4	49.8	4.1	5.0
Chrysene	39.3	38.7	35.5	51.4	9.2	8.8
Benzo(b/k)fluoranthene	45.5	43.5	39.3	60.6	10.2	7.4
Benzo(a)pyrene					5.2	4.1
Indeno(123-cd)pyrene					3.4	
Benzo(ghi)perylene					4.0	
Hydrocarbons c15-c30	(5) 16350	22050	25840	11290	19600	35000

Another set of samples were also sent to De Monfort University for analysis and had wider range of organics being analysed. Table 13 shows the different compounds found in the samples extracted with ethyl acetate and hexane.

Table 13: Organic compounds in sediments, solvents: ethyl acetate and hexane, (De Montfort University analysis)

Compound Name	Relative comp%	Compound Name	Relative comp %
ETHYL ACETATE:		Benzene, 1,1'-(3-methyl 3-dimethyl	15.5
Styrene	2.1	1, 3-Butadiene, 1,4-diphenyl-, (E,E)-	7.3
Benzene ethoxy-	1.3	Naphthalene, 1,2-dihydro-4-phenyl-	16.8
Dibenz[ah]anthracene- tetrahydro	2.1	Adamantane-1(3dichloropropyn-1-yl)	1.7
Benzene, 2-chloro-1,3,5-trimethyl-	0.4		
Naphthalene	0.3		
Naphthalene, 1,2,3-triphenil-	1.0	**HEXANE:**	
1-Dodecene	0.2	Heptane,2,4-dimethyl-	1.0
1,4-Methanonaphthalene	0.2	Benzene,1-methyl-3-(1-methylethyl-	0.5
Naphthalene, 1-methyl-	0.5	1,3,8-p-Menthatriene	4.1
6,7,8-Trimethyl, dibenzo -xanthene	0.4	Dibenz[a,H]antracene,5,12-diphenyl"	2.4
Naphthalene, 1,4-dimethyl-	0.5	Naphthalene, 2-methyl	0.6
Acenaphthene	1.2	Benzene, 1,2,4,5-tetramethyl-	0.4
Decane, 2,4,6-trimethyl-	1.2	Naphtalene,2,7-dimethyl	0.8
Naphthalene, 2-(1-methylethyl)-	0.3	Acenaphthene	2.8
Dibenzofuran	0.9	Dibenzofuran	1.9
Fluorene	0.4	2-Chloro-diphenyl-methane	1.9
2-Ethyl-1-dodecanol	2.4	Nonadecane	5.5
Styrene	3.9	1-hexadecanol, 2-methyl	12.8
Naphthalene, 1-4hydro-2-phenyl	0.6	1,1'-Biphenyl, 2,2',3,4,4',5,6,6'-octachloro	2.8
2-Hexyl-1-octanol	5.4	Anthracene	7.9
Benzene,1,1'-(1,2-cyclobutanediyl)	9.2	9,9'-Biphenanthrene, octacosahydro-	2.5
Anthracene	6.1	Docosane	9.0
Docosane	1.7	Fluoranthene	15.2
1,1'-Biphenyl, 2,3,3'-trichloro-	1.7	Pyrene	11.9
Fluoranthene	7.4	Phenanthrene	12.7
Pyrene	5.7	1,1'-Biphenyl, 2,2',3,3',4,5',6,6'-octachloro-	2.6

5.8 PARTICLE SIZE ANALYSIS

Samples for particle size analysis were prepared prior to analysis. The samples were sieved through a 2.0 mm sieve first, followed by a 1.0 mm sieve. Table 14 shows the mass of each fraction. The fraction of samples less than 1.0 mm was analysed by the Mastersizer and, after analysis, the sand fraction was readjusted.

Table 14: Particle size pre-analysis. Mass in gram (g)

Particle size sample preparation:				
Sample		< 1.0 mm	> 1.0 mm	TOTAL
Belper Bridge	TOP	17.8	1.9	19.7
	MIDDLE	19.1	1.3	20.1
	BOTTOM	23.9	1.3	25.3
Titford	TOP	13.7	2.1	15.8
	MIDDLE	15.3	0.4	15.7
	BOTTOM	11.2	5.3	16.5
Horseley Fields Bridge	TOP	9.0	0.9	9.9
	MIDDLE	12.2	0.1	12.3
	BOTTOM	11.5	0.6	12.1

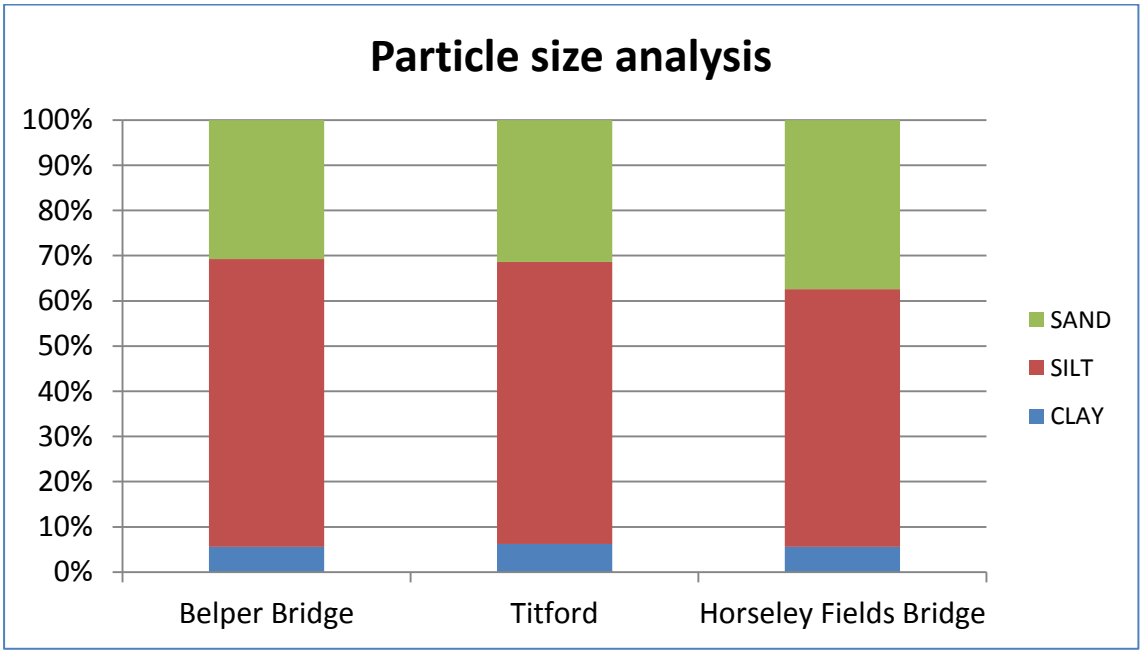


Figure 37: Clay, silt and sand fractions for Belper Bridge, Titford and Horseley Fields Bridge.

5.8.1 Belper Bridge

Figure 37 shows the percentage of clay, silt and sand for the three sites. Each sample point in the sediment tanks were analysed 4 times to reduce errors. Belper Bridge had similar particle size composition for all three sample points: top, middle and bottom. The top sample point had 6.0% clays, 64.0% silts and 30.0% sand. The middle sample point had a similar distribution with 5.0% clays, 62.0% silts and 33.0% sand and the bottom sample point had 6.0% clays, 65.0% silts and 29.0% sand which was lower than the top and middle sample point.

5.8.2 Titford

Titford (Figure 37) had a slightly different composition to Belper Bridge. The top sample point had 6.0% clay, 64.0% silts and 30.0% sand. The middle sample point had more silt than clay with 73.0% silt and 6.0% clays. The sand fraction was lower in this sample point with only 20.0% of the total composition. The bottom sample point had more sand, as expected, but was still mainly composed of silts and clays, with around 6.0% clays and 49.0% silts. The sand fraction in this sample point made up 45.0% of the total composition.

5.8.3 Horseley Fields Bridge

Horseley Fields Bridge (as shown in Figure 37) had a similar particle size distribution as Titford with higher clay and silt fraction for the first two sample points and higher sand fraction for the bottom sample point. The sediments consisted of 5.0% clays, 62.0% silts and 32.0% sand for the top sample point, while the middle sample point consisted of 6.0% clays, 57.0% silts and 36.0% sand. The bottom sample point had 5.0% clays, 51.0% silt and 43.0% sand, the highest sand fraction between the sample points.

5.9 X-RAY DIFFRACTION

Table 15: XRD results for three sites with match scores (MS)- highest match scores in green and lowest in yellow

MS	Belper Bridge	MS	Titford	MS	Horseley Fields Bridge
16.1	vivianite	13.3	tricalcium aluminate	12.4	tricalcium aluminate
14.8	tricalcium aluminate	10.8	calcium tartrate hydrate	12.1	sodium copper phosphate
14.5	calcium aluminium oxide	10.3	dipotassium pentabromouranate	8.9	sodium cobalt phosphate
12.4	aluminium calcium oxide	9.1	zinc vanadium oxide	8.4	chloritoid-A
11.9	baricite	8.9	gamma-gueggenite	7.9	telluropalladinite
9.3	dipotassium pentabromouranate	8.6	margarite-2m1	7.9	aluminium sulphide
9.2	aluminium oxide	8.5	carlosturanite	7.7	calcium aluminium oxide
8.9	iron oxide	8.2	calcite	7.6	calcite
8.6	annabergite, magnesian	7.9	annabergite, magnesian	7.5	huntite
8.3	cobalt arsenate hydroxide	7.8	sodium titanium vanadium oxide	6.9	iron titanium hydride
7.7	barium zinc hydroxide	7.4	calcium nickel silicate	6.6	quartz
7.6	rankinite	6.8	quartz	6.5	nickel phosphate
7.4	montbrayite	6.7	copper magnesium oxide	6.2	tsumcorite
7.3	labradorite	6.6	chloritoid-A	5.9	calcium cobalt silicate
7.2	calcite	6.5	bideauxite	5.8	rammelsbergite
7.2	chloritoid-A	6.4	aluminium calcium manganese	5.8	aluminium oxide
7.0	adamite	6.2	sodium manganese oxide	5.6	strontium cobalt oxide
6.6	quartz	5.8	perovskite	5.5	hedenbergite
6.5	hedenbergite	5.8	iron strontium phosphide	5.5	aluminium titanium
6.3	nickel phosphate	5.4	calcium aluminium oxide	5.0	copper selenide sulphide
6.2	chloritoid	5.2	gaspeite	5.0	zinc titanium oxide
5.6	potassium hydrogen phosphate	5.2	sodium phosphate oxide	5.0	kutnohorite, magnesian
5.4	sodium calcium aluminium oxide	5.0	muscovite	4.9	rucklidgeite
5.3	cobalt phosphide	4.9	iron oxide	4.8	northrupite

5.9.1 Belper Bridge

Table 15 shows the XRD match results for the three sites. The match score and intensity for the compounds/minerals in each sample point in the sediments can be found in Appendix 1.10. The major compounds present in the sediments were iron oxides, silicon oxide, quartz, calcite, hydroxides and sulphides, as expected in canal sediments.

5.9.2 Titford

Table 15 shows the XRD results for Titford. The results were similar to Belper Bridge with oxides, hydroxides and sulphides being the most abundant.

5.9.3 Horseley Fields Bridge

Table 15 also shows the XRD results for Horseley Fields Bridge. The matching compounds/minerals are similar to the other sites with oxides, hydroxides, silicates and sulphides as the major constituents of the sediments.

5.9.4 XRD spectra for Belper Bridge, Titford and Horseley Fields Bridge

Figure 38 shows the spectra for the top, middle and bottom sample points for the three sites. As it can be seen there are major similarities for the oxides, sulphides and silicates, but distinct differences between the sites. Horseley Fields Bridge has specific peaks towards the end of the spectra which are not present in the other two sites and Belper Bridge has specific peaks around 13 (2θ).

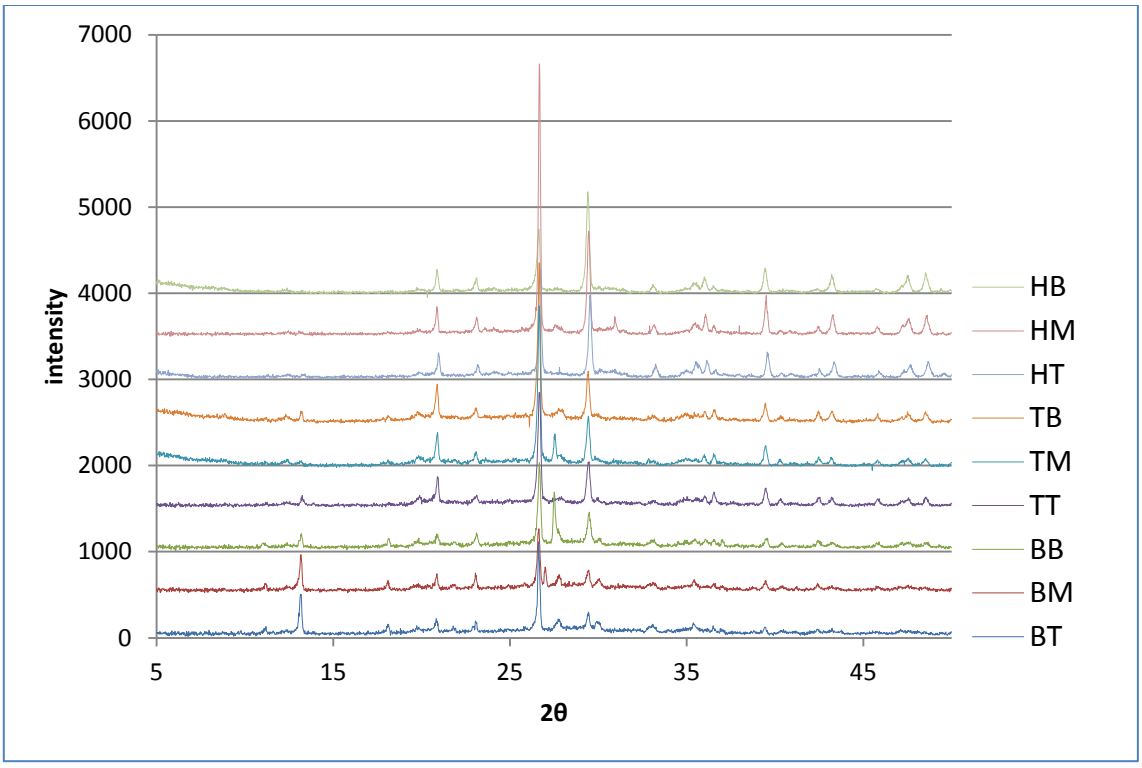
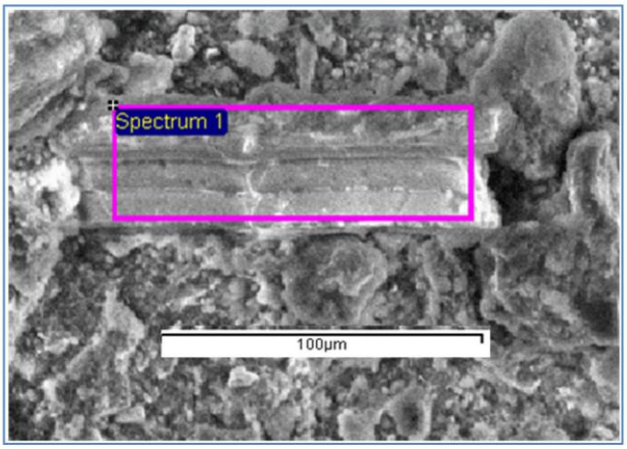


Figure 38: XRD spectra for the three sample points at the three sites (HB: Horseley Fields bottom, HM: Horseley Fields middle, HT: Horseley Fields Top, TB: Titford Bottom, TM: Titford Middle, TT: Titford Top, BB: Belper Bottom, BM: Belper Middle, BT: Belper Top).

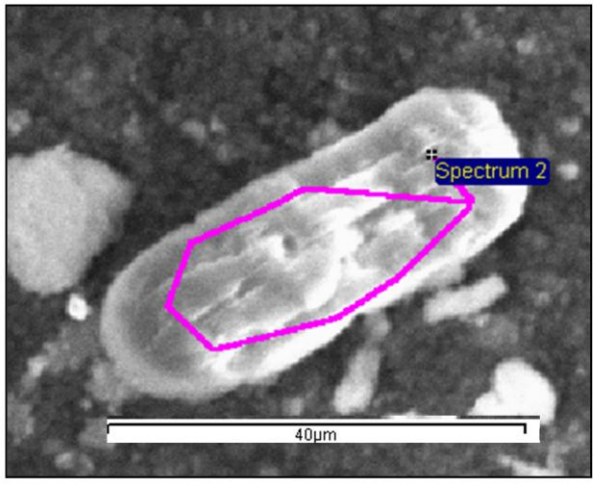
5.10 SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE X-RAY ANALYSIS (SEM-EDX)



Element	Weight%	Atomic%
C	39.5	55.2
O	28.9	30.3
F	0.8	0.7
Mg	0.2	0.1
Al	0.9	0.5
Si	2.2	1.3
P	6.5	3.5
S	0.9	0.4
K	0.1	0.0
Ca	15.0	6.2
Mn	0.4	0.1
Fe	3.1	0.9
Cu	0.2	0.1
Zn	0.3	0.1

Figure 39: SEM micrograph and EDX table showing a general analysis of a possible calcium carbonate with high proportion of Ca, C and O.

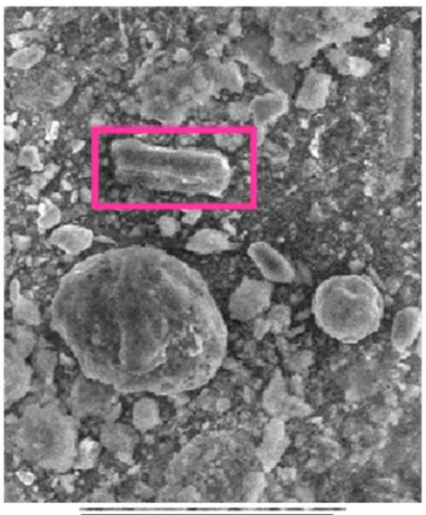
The SEM-EDX analysis showed that all the samples contained high proportions of carbon as shown on Figure 39. This was possibly due to the high organic content of the sediment and not the carbon stub. The mineralogy of the different constituents in the sediments were more complex than expected and the sediments being so mixed up, it was difficult to determine which part of the samples were coated by, or attached to, organic matter.

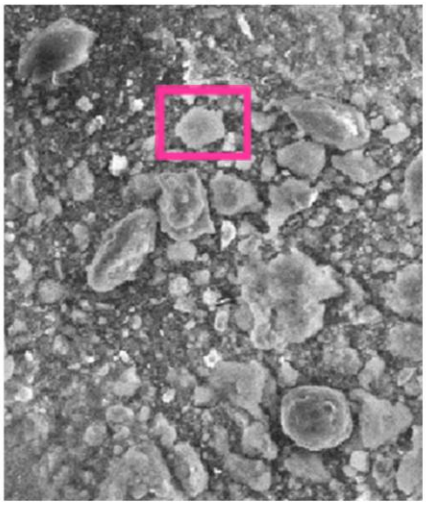


Element	Weight%	Atomic%
C	37.7	50.1
O	42.5	42.4
Na	0.2	0.1
Mg	0.5	0.3
Al	0.3	0.2
Si	0.5	0.3
P	5.3	2.7
S	0.2	0.1
K	0.0	0.0
Ca	0.5	0.2
Mn	0.3	0.1
Fe	11.2	3.2
Cu	0.1	0.0
Zn	0.1	0.0

Figure 40: SEM Micrograph and EDX table showing a possible iron phosphate.

The SEM-EDX in Figure 40 show one of the more common mineral in the sediments. Its high percentage of iron, phosphorus and oxygen suggests that it is an iron phosphate if the carbon concentration is not taken into consideration.





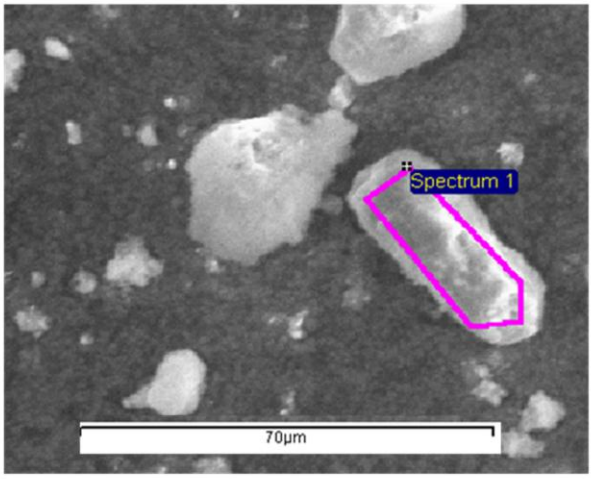
Element	Weight%	Atomic%
C	44.2	57.2
O	34.8	33.8
Mg	0.3	0.1
Al	2.1	1.2
Si	3.9	2.2
P	2.2	1.1
S	1.9	0.9
K	0.3	0.1
Ca	2.8	1.1
Ti	0.1	0.0
Mn	0.1	0.0
Fe	5.4	1.5
Cu	0.5	0.1
Zn	1.0	0.2

C	32.7	47.1
O	34.2	37.0
F	1.0	0.9
Mg	0.4	0.3
Al	2.6	1.7
Si	5.7	3.5
P	4.4	2.4
S	1.6	0.9
Cl	0.1	0.0
K	0.4	0.1
Ca	5.5	2.4
Ti	0.1	0.0
Cr	0.1	0.0
Mn	0.1	0.0
Fe	8.2	2.5
Cu	0.5	0.1
Zn	1.7	0.4

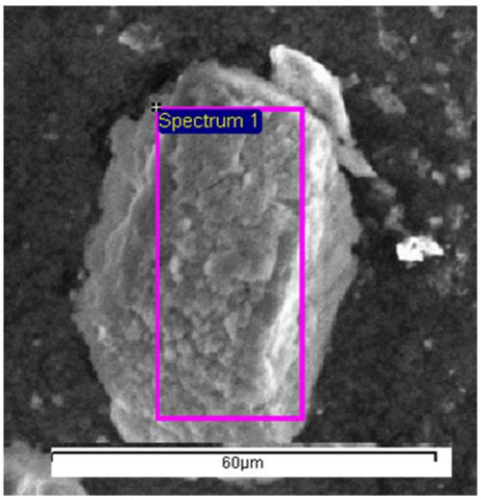
Figure 41: SEM Micrographs and EDX tables showing two analyses with similar composition possibly of an iron compound or aluminosilicate.

Figure 41 shows two samples from the same stub with the backscatter detector which helps pinpoint areas of interest within the samples. Both samples had various concentrations of different elements and thus an exact identity could not be determined. The top picture has Fe, Ca, Si, Al, S, Zn, P, C and O. These could be iron oxide, iron phosphate, iron carbonate or aluminium silicate. The second picture has similar concentrations of the same metals, but the

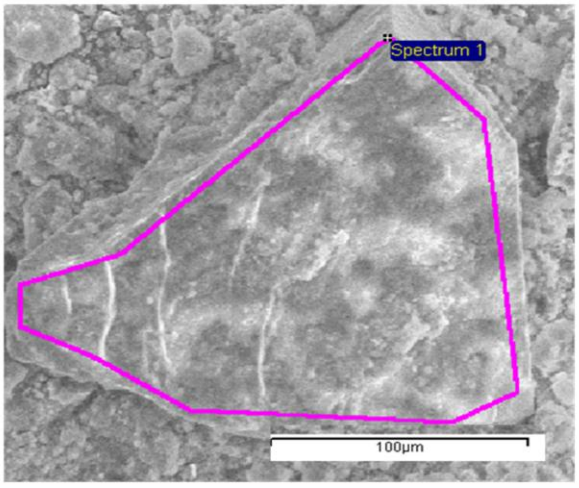
sample has a very different shape and texture. Figure 42 show possible iron oxides mixed with phosphates and silicates.



Element	Weight%	Atomic%
C	47.4	60.0
O	35.5	33.7
Na	0.2	0.1
Mg	0.3	0.2
Al	0.4	0.2
Si	0.7	0.3
P	4.0	1.9
S	0.4	0.2
K	0.1	0.0
Ca	0.7	0.3
Mn	0.1	0.0
Fe	9.6	2.6
Zn	0.2	0.1



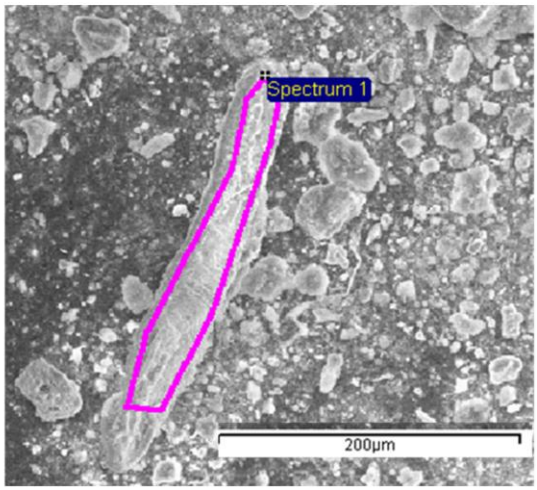
Element	Weight%	Atomic%
C	46.6	60.2
O	33.6	32.6
Na	0.2	0.1
Mg	0.3	0.2
Al	0.4	0.2
Si	0.7	0.3
P	4.2	2.1
S	0.4	0.2
K	0.0	0.0
Ca	0.8	0.3
Mn	0.4	0.1
Fe	11.8	3.3
Cu	0.1	0.0



Element	Weight%	Atomic%
C	19.6	32.0
O	37.0	45.4
Mg	0.5	0.4
Al	3.6	2.6
Si	13.1	9.2
P	2.1	1.3
S	0.6	0.4
K	0.6	0.3
Ca	2.6	1.2
Ti	0.2	0.1
Mn	0.8	0.3
Fe	18.3	6.4
Zn	0.5	0.1

Figure 42: SEM micrographs and EDX tables of three samples showing iron compounds but with different associations, such as phosphates and silicates with different textures and morphologies.

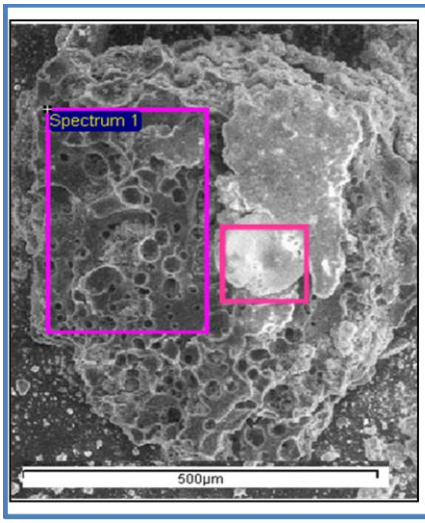
Figure 43 shows a possible aluminosilicates most probably with a coating of organic matter as suggested by the high concentration of carbon and oxygen.



Element	Weight%	Atomic%
C	28.2	39.1
O	42.7	44.5
Na	0.2	0.1
Mg	0.1	0.1
Al	11.8	7.3
Si	11.4	6.7
P	0.8	0.4
S	0.4	0.2
K	0.4	0.2
Ca	0.9	0.4
Ti	0.1	0.0
Fe	1.9	0.5
Cu	0.1	0.0
Zn	0.4	0.1

Figure 43: SEM micrograph and EDX data showing a possible aluminosilicate coated by organic matter.

Figure 44 shows part of the sediments with two spectra with similar compositions. The second spectrum is flatter and more conductive than spectrum 1 and gives a better overview of the different elements present in the sediments.

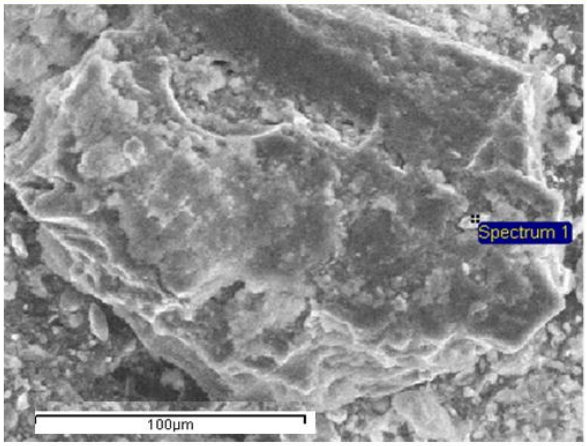


Element	Weight %	Atomic %	Element	Weight%	Atomic %
C	68.5	78.5	C	60.5	71.5
O	20.0	17.2	O	26.2	23.2
Mg	0.1	0.1	Mg	0.2	0.1
Al	1.2	0.6	Al	1.3	0.7
Si	2.3	1.1	Si	2.3	1.2
P	0.9	0.4	P	1.6	0.7
S	0.8	0.3	S	1.1	0.5
K	0.3	0.1	Cl	0.0	0.0
Ca	1.8	0.6	K	0.2	0.0
Ti	0.1	0.1	Ca	2.3	0.8
Fe	3.1	0.7	Ti	0.1	0.0
Zn	0.3	0.1	Fe	3.1	0.8
			Zn	0.4	0.1

Figure 44: SEM micrograph and EDX data showing two spectra for the same sample, spectra 1 on the left and spectra 2 on the right, possibly a zinc sulphate attached to an iron oxide.

Figure 45 shows two spectra, the first one most probably being a zinc sulphate attached to the larger cluster and the second one showing an overall analysis which could be a mix of iron

oxides and aluminosilicates. More SEM micrographs and EDX data are presented in Appendix 1.3.



Element	Weight%	Atomic%	Element	W%	A%
Spec 1			**overall**		
C	46.7	64.8	C	57.7	69.6
O	23.3	24.3	O	26.1	23.7
Mg	0.2	0.1	F	0.6	0.5
Al	1.2	0.7	Mg	0.2	0.1
Si	1.8	1.1	Al	1.7	0.9
P	1.0	0.5	Si	2.9	1.5
S	4.6	2.4	P	1.7	0.8
Cl	0.1	0.1	S	1.1	0.5
K	0.1	0.1	Cl	0.1	0.0
Ca	1.4	0.6	K	0.2	0.0
Fe	3.5	1.0	Ca	2.4	0.8
Cu	1.4	0.3	Ti	0.1	0.0
Zn	14.1	3.6	Fe	3.7	0.9
			Cu	0.2	0.1
			Zn	0.8	0.1

Figure 45: SEM micrograph showing a possible zinc sulphate (left) and overall analysis of the sample (right 3 columns).

5.11 Statistical analysis of data

5.11.1 pH vs. site

The pH for the three sites did not vary significantly between the replicates ranging between 6.5 and 7.5 for all three sites. Two-way Anova for pH showed that the factor 'site location' accounts for 14.7% of the total variance, which meant that the effect of site was considered extremely significant ($P<0.0001$). This means that the three sites have very different pH-Redox values between sites, but are similar in terms of the relationship between these two factors. Sediments for all three sites remained anoxic even after being dredged. The oxidised sample point was only a few millimetres thick and formed a reddish grey film at the surface of the

tanks. Titford and Horseley Fields Bridge have a positive correlation, whereas Belper Bridge has a negative correlation. It has been well established now that pH and Redox are correlated (Sparks, 1999) and in this case the three sample sites have Pearson correlation coefficients (r) of 0.85 for Horseley Fields (n=300, p= 0.03), -0.81 for Belper Bridge (n=300, p= 0.05) and 0.87 for Titford (n=300, p= 0.03). The results for Belper Bridge are different to the other two sites (Figure 46).

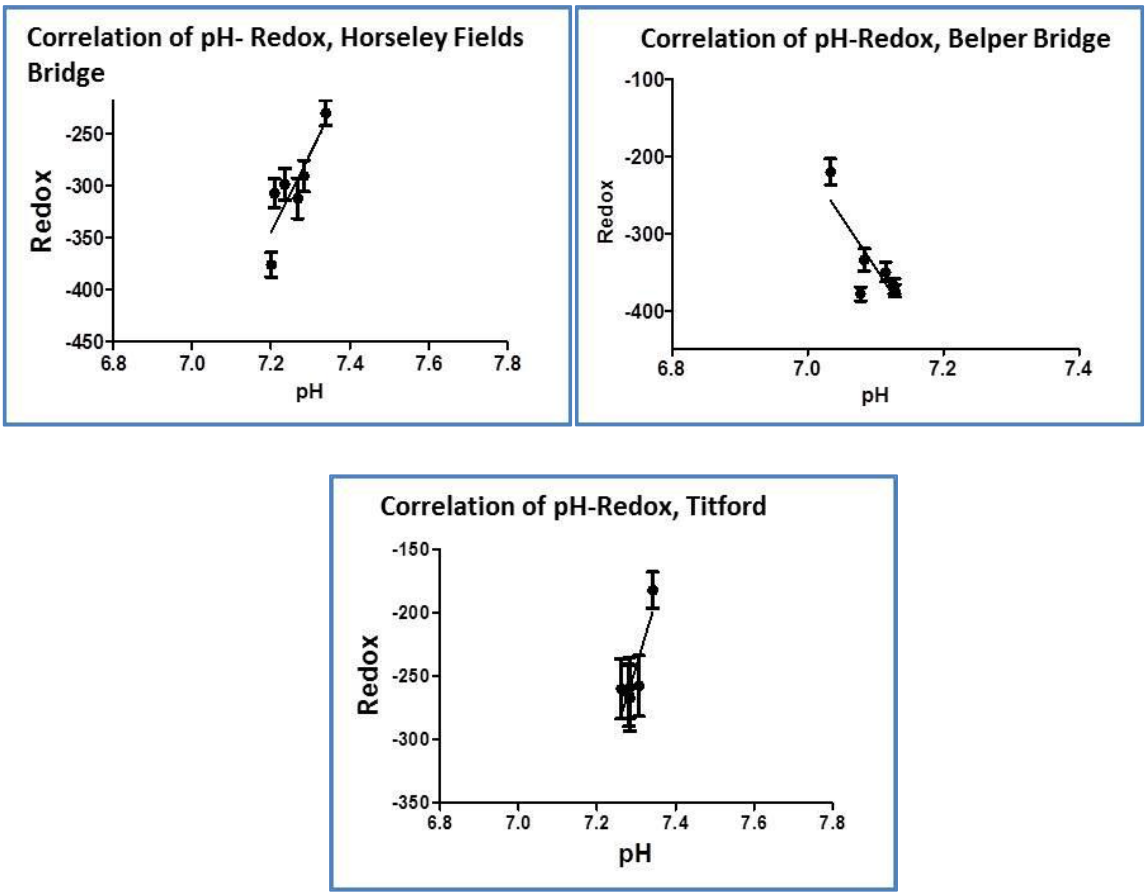


Figure 46: Correlation of pH and Redox for Belper Bridge, Titford and Horseley Fields Bridge.

5.11.2 Particle size vs. site

Particle size is significantly different between sites and accounts for 93.7% of the total variance with P<0.0001. Moreover, the statistical analysis show that the effect of 'site location' is not significant (P=1.0, F=0.0001 dFn=2.0, dFd=12.0). The P value in the two-way ANOVA analysis is determined from the F values. Each F ratio is the ratio of the mean-square value for that source of variation to the residual mean square. The F ratio is used to test for the null

hypothesis, which suggests there are no interactions between rows and columns in the data. An F value close to 1.0 suggests that the null hypothesis is true.

5.11.3 XRF vs. Particle size

The data from the XRF and particle size were analysed using two way ANOVA followed by Dunn's Multiple Comparison Test. This computes the associations of the different particle size fractions and their significant association with the main PHEs, as shown in Table 16. From the Dunn's comparison Test, it can be deduced that the main PHEs distribution that could be influenced by particle size are Cr, Cu, Pb, and Zn for clay followed by Cu, Pb and Zn for silt and sand.

Table 16: Dunn's multiple comparison test (ns= not significant)

Dunn's Multiple Comparison Test	Significant?
CLAY vs Cd	ns
CLAY vs. Cr	P < 0.050
CLAY vs. Cu	P < 0.001
CLAY vs. As	ns
CLAY vs. Pb	P < 0.001
CLAY vs. Zn	P < 0.001
CLAY vs. Ni	ns
SILT vs. Cd	ns
SILT vs. Cr	ns
SILT vs. Cu	P < 0.001
SILT vs. As	ns
SILT vs. Pb	P < 0.010
SILT vs. Zn	P < 0.001
SILT vs. Ni	ns
SAND vs. Cd	ns
SAND vs. Cr	ns
SAND vs. Cu	P < 0.001
SAND vs. As	ns
SAND vs. Pb	P < 0.010
SAND vs. Zn	P < 0.001
SAND vs. Ni	ns

5.11.4 Correlation between PHEs

The results for the total concentration of PHEs in the sediments have been analysed using the Bonferroni post test to determine correlations between elements. Table 17 shows the major associations for all three sites. Zinc was the only element strongly associated (P<0.001) with the other PHEs, such as chromium, cadmium, nickel, arsenic, lead and moderately correlated (P<0.05) with copper. There was little difference between the sample points for the correlations of these PHEs, except for the bottom sample point between zinc and lead.

Table 17: Major correlations between elements for Belper Bridge, Titford and Horseley Fields Bridge

	sample point	Difference	t	P value
Zn vs. Cr	top	9625	4.484	P<0.001
	middle	9365	4.363	P<0.001
	bottom	9132	4.254	P<0.001
Zn vs. Ni	top	9755	4.545	P<0.001
	middle	9491	4.422	P<0.001
	bottom	9250	4.309	P<0.001
Zn vs. Cu	top	6533	3.044	P < 0.05
	middle	6470	3.014	P < 0.05
	bottom	6345	2.956	P < 0.05
Zn vs. As	top	-9902	4.613	P<0.001
	middle	-9639	4.491	P<0.001
	bottom	-9396	4.378	P<0.001
Zn vs. Cd	top	-9921	4.622	P<0.001
	middle	-9660	4.500	P<0.001
	bottom	-9413	4.386	P<0.001
Zn vs. Pb	top	-8816	4.107	P<0.001
	middle	-8574	3.995	P<0.001
	bottom	-8365	3.897	P<0.010

5.11.5 Between sites

Variation between the concentrations of the PHEs in the sediments were considered extremely significant (P<0.0001) for all the PHEs. The results were also extremely significant for pore water elemental concentration (P<0.0001) and for pore water ionic concentration (P=0.0007). The results were extremely significant for Redox (P<0.0001), but not quite significant for pH (P=0.054).

THIRD TRIAD: BIOLOGICAL CHARACTERISATION

CHAPTER 6

"The heights by great men reached and kept were not obtained by sudden flight, but they, while their companions slept, were toiling upwards in the night" – Thomas S. Monson

CHAPTER 6

BIOLOGICAL CHARACTERISATION

6.1 THE THIRD TRIAD (BIOLOGICAL CHARACTERISATION)

Sediments contain a wide variety of bacteria mostly adapted to anoxic conditions. These can affect the various chemical processes operating in the sediments. Dean-Ross et al. (2002) demonstrated the capability of bacteria to degrade PAHs and affect the mobility of PHEs. Microbiological activity can play a role in oxidising sulphide minerals to sulphates and in the process produce acids that can lower the pH of the system, but this is often buffered by calcite and carbonates in the sediments (Gomez *et al.*, 1999). Nevertheless, it is known that bacteria can reduce PHE concentrations in aqueous solutions by assimilating metals into their structure due to their functional groups, such as carboxyls, sulphydryl, amino and carbonyl amongst others (Wang and Chen, 2008).Therefore, this brief investigation aims to assess whether further research needs to be undertaken on canal sediments and assessing the success or otherwise of any potential remediation strategies using zeolites in the presence of bacteria.

6.2 METHODOLOGY

6.2.1 Colony counts

In order to determine the approximate bacterial population present in the sediments, viable counts of colonies were undertaken. Viable counts are based on the assumption that each bacterium placed on agar plates would multiply and produce colonies. Each colony was formed from one colony forming unit (C.F.U.), which is equivalent to a microbial cell. There are different ways to estimate the population of bacteria in a sample, for example, counting the colonies on agar plates and thus estimating the number of C.F.U of bacteria /g of sediments.

To obtain isolated colonies, a serial dilution methodology was undertaken (from concentrated to 10^{-1}, 10^{-2}, up to 10^{-8}). Eight test tubes were filled with 4.5 ml ¼ ringer solutions. 0.5 gramme of sediments were added to the first test tube and the mixture was thoroughly mixed with the aid of a vortex mixer. 500 ml of the solution was removed using a Finn pipette and mixed with the second test tube content. Once this was thoroughly mixed, 500 ml of this solution was mixed with the next test tube content and this was repeated until 8 serial dilutions. 0.1 ml of solution from the first test tube was then transferred to an agar plate (Tryptic [Trypticase] Soy Agar (30.0 g TSA and 15.0 g of agar mixed with 1 litre distilled water)) using a finn pipette

using aseptic techniques. The solution was spread over the agar plate using an alcohol-flamed glass spreader. The plates were carefully labelled and incubated for 24 hours at 28 °C.

The number of colonies on each plate was counted after 24 hours (Table 18). Since it was thought canal sediments would contain different types of bacteria, it was necessary to identify the different types of bacteria present. Gram staining is the first step in doing so and is a valuable method commonly used to differentiate bacteria into two different categories (Gram-positive and Gram-negative) based on the physical and chemical properties of their cell wall. The different types of bacteria were identified on the plates. Using a sterilised inoculation loop, a drop of water was added onto a slide. A small amount of the bacteria was transferred with an inoculation loop and smeared over the slide. This was left to dry for one minute. The slide was then moved swiftly over a Bunsen flame for a short period time to fix the bacteria. Crystal violet stain was added to the slides and left for one minute. The stain was then washed off with water and Grams iodine stain was added and left for 2 minutes. The excess solution was then washed off with ethanol, immediately followed by water. Safranin stain was then added and left for another minute. This was then washed off with water and the slide was dried using filter paper (blot dry and not rubbed).

6.2.2 Fatty acid extraction for bacterial identification

The bacterial species cultured from the sediments were identified using the methodology presented by Sasser (1990), who has routinely used fatty acids to identify anaerobic bacteria. The methodology extracts fatty acids from lipids which are then analysed and identified by GC-MS.

The extraction process involves four reagents; Reagent 1 (45.0 g sodium hydroxide, 150 ml methanol, 150 ml distilled water), Reagent 2 (325.0 ml of 6.0 N hydrochloric acid, 275.0 ml methyl alcohol), Reagent 3 (200.0 ml hexane, 200.0 ml methyl tert-butyl ether) and, Reagent 4 (10.8 g sodium hydroxide, 900.0 ml distilled water).

Bacteria were cultured on Trypticase Soy Broth Agar (TSBA) (30.0 g Trypticase Soy Broth and 15.0 g of Agar) by quadrant streaking and left to incubate at 28 °C and were harvested after 24 hours.

Bacteria were harvested (40.0 mg) from quadrant 3 using a 4.0 mm loop and transferred to a sterile culture tube. 1.0 ml of reagent 1 was then added to each culture tube and vortexed for 10

seconds. The tubes were then transferred to a water bath at 100 °C for 5 minutes followed by vortexing for a further 10 seconds before they were returned to the boiling water bath for 25 minutes.

The culture tubes were allowed to cool down after which 2.0 ml of reagent 2 was added. The tubes were then vortexed for 10 seconds and heated at 80 °C (+/-1 °C) for 10 minutes (+/- 1 minute) followed by rapid cooling in a freezing water bath.Following this, 1.25 ml of reagent 3 were added to the tubes, which were then tumbled on a clinical rotator for 10 minutes. The aqueous phase (lower) of the solution was pipetted out and discarded. Reagent 4 (3 ml) was then added to the tubes and tumbled for a further 5 minutes. Finally, 2/3 of the organic phase (top layer) was transferred into a GC vial ready for GC-MS analysis and sent to Poland where they were analysed by Professor Zofia Piotrowska-Seget at the university, Uniwersytet Slaski, Poland.

6.3 RESULTS

6.3.1 Colony counts

Table 18 shows the colony counts for the Belper Bridge, Titford and Horseley Fields Bridge sites. The bacterial colonies were too numerous to count at dilution factor 10^{-1} and gradually decreased to zero at higher dilution factors. The colony forming units (C.F.U) per gram were higher at Titford, followed by Horseley Fields Bridge and finally Belper Bridge.

Table 18: Colony counts for samples from Belper Bridge, Titford and Horseley Fields Bridge (TNTC: too numerous to count)

DILUTION	BELPER BRIDGE	TITFORD	HORSELEY FIELDS BRIDGE
10^{-1}	TNTC	TNTC	TNTC
10^{-2}	30	115	90
10^{-3}	4	9	7
10^{-4}	2	1	1
$10^{-5 \text{ to } -8}$	0	0	0
No. of colonies / 1ml	BELPER BRIDGE	TITFORD	HORSELEY FIELDS BRIDGE
10^{-1}	TNTC	TNTC	TNTC
10^{-2}	300	1150	900
10^{-3}	40	90	70
10^{-4}	2	10	5
Number of colonies in 1ml undiluted suspension taking 10^{-2} as most viable plates:			
C.F.U/g :	Belper: 3×10^4	Titford: 1.15×10^5	Horsley Fields: 9×10^4

6.3.2 Belper Bridge

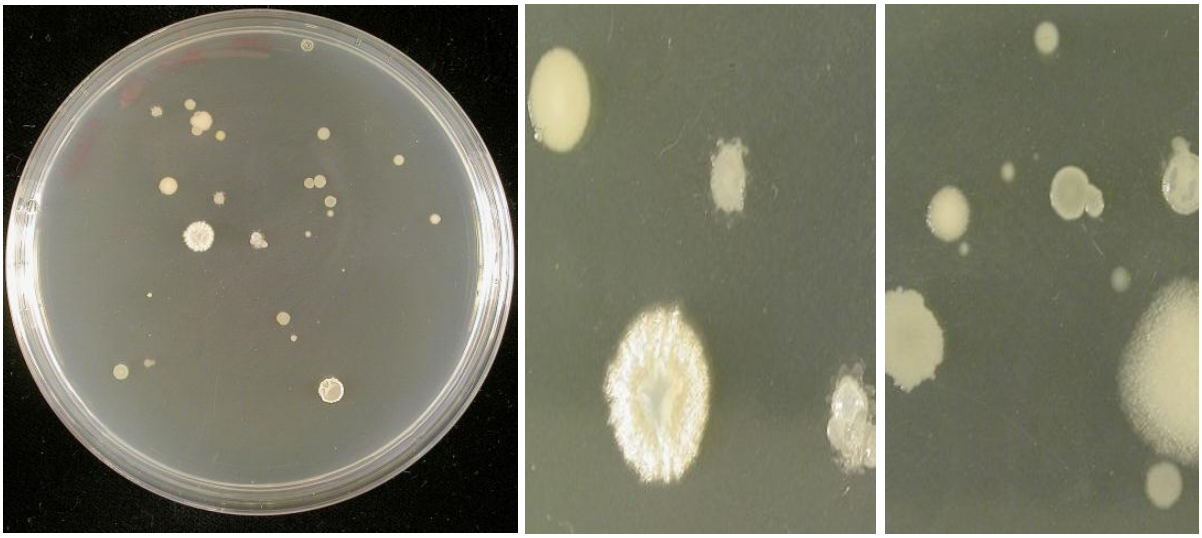


Plate 7: Bacterial colonies on agar plate for Belper Bridge.

The colonies from Belper Bridge were mainly circular with different textures for the different species. There were three distinct species on all the growing media, one with a yellowish colour, one with a textured surface (see middle image on Plate 7) and one grey with a glossy texture.

6.3.3 Titford

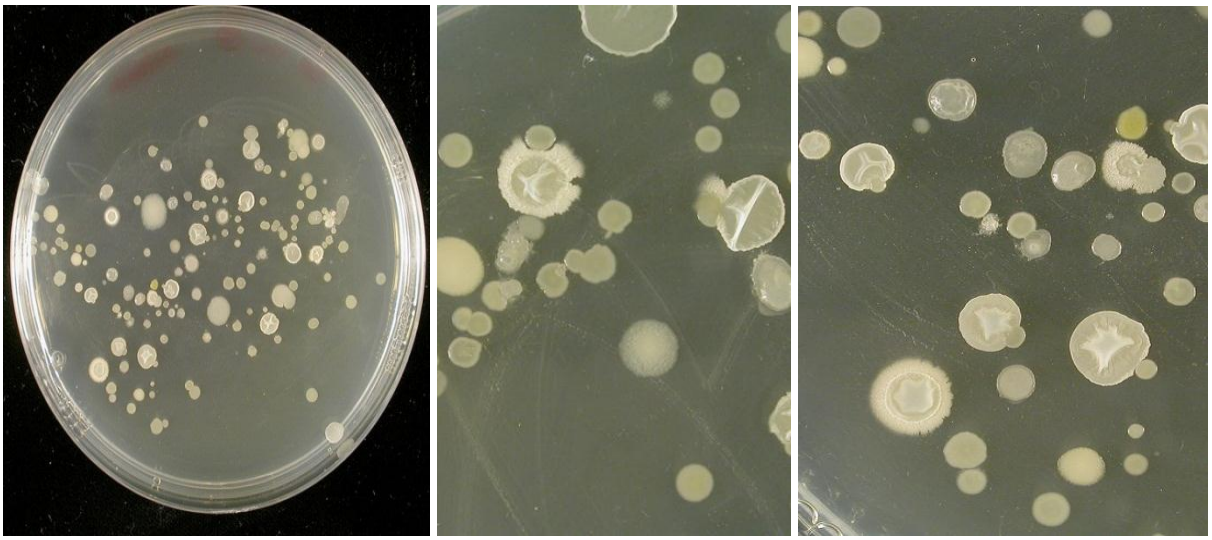


Plate 8: Bacterial colonies on agar plate for Titford.

Titford samples had similar species, but in higher numbers and with larger colonies (Plate 8). The most abundant species was the glossy grey species and the larger textured species. Titford sample plates showed faster growth over 24 hours compared to the other two sites.

6.3.4 Horseley Fields Bridge

Horseley Fields Bridge showed similar bacterial species compared to the other two sites, but in lower numbers and in smaller colonies, as shown on Plate 9.

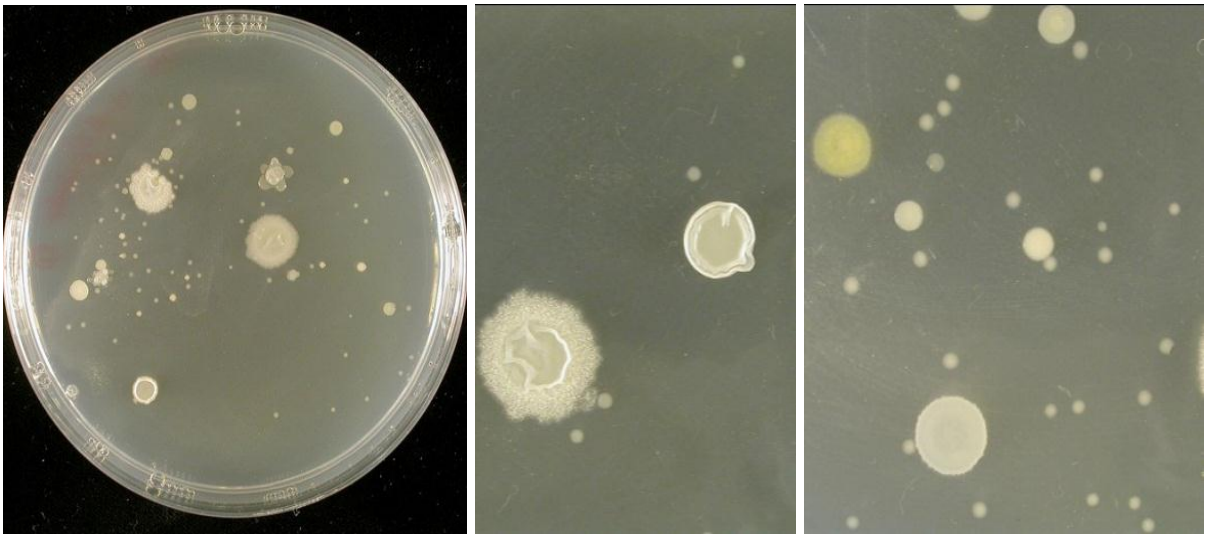


Plate 9: Baterial colonies on agar plates for Horseley Fields Bridge.

More plate pictures are presented in Appendix 1.6 for all three sites.

6.3.5 Bacterial identification

The results from the GC-MS showed 17 possible matches, but the six presented below had match scores above 95% and so the following bacteria were identified with confidence as the species present on the cultures. There is a paucity of literature regarding these bacterial species and their presence in canal sediments. Some of these bacteria could be sulphate-reducing bacteria (SRB) which would explain their presence in the sediments, since sulphates were present in the sediments (Section 5.5). The bacteria species are anaerobic (although cultured under aerobic conditions) and so could have an effect on PHE mobility, as some bacteria species can incorporate PHEs in their structure.

- *Bacillus-megaterium*
- *Bacillus-alcalophilus*
- *Brevibacillus-parabrevis*
- *Staphylococcus-vitilinus*
- *Staphylococcus-sciuri*
- *Staphylococcus-lentus.*

The presence of anaerobic bacteria in canal sediments and their effects on PHEs are broadly unknown. The six bacteria species identified here were grown on TSA media, which is the typical growth media used for unknown bacterial colonies. It is possible that some bacteria in the sediments could grow on other growth media. Therefore, more research needs to be conducted on the identification of the bacterial species in the canal sediments as the total species population is most probably not limited to the six identified here.

6.4 IMPLICATIONS OF BACTERIAL IDENTIFICATION FOR CHARACTERISATION AND REMEDIATION OF CANAL SEDIMENT

The sequential extraction results showed the different fractionation of PHEs in the sediments (Section 5.2). PHEs can be associated with the soluble phases or the stable phases. From the sequential extraction results and ICP results, it was deduced that PHEs were mainly associated with the most stable phases. The bacterial colonies in Section 6.3.5 can have an important effect on binding of PHEs as described by Selenska-Pobell *et al*. (1999), who outlined the binding capabilities of *Bacillus sp*. and their presence in contaminated waters. Some PHEs are irreversibly bound by *Bacillus sp.* bacteria, such as Al and Cd, which would hinder any remediation endeavours using zeolites. The research also outlines the identification of strains which can adapt to harsh environments such as contaminated waters and adapt to their new environments by binding PHEs. Moreover, bacteria in the sediments could have absorbed and immobilised PHEs that were previously in solution resulting in the lower concentrations of these PHEs in the ICP results. In this research, the results of the ICP could have been lower than the actual concentration of PHEs in solution if PHEs were absorbed and assimilated by bacteria. In terms of characterisation, the effect of bacteria is not crucial as long as the PHEs are known to be in stable phases. On the other hand, if PHEs are bound to bacteria, they might be potentially more mobile if the bacteria die or if the bacteria release PHEs if conditions such as pH change. Some species of bacteria can thrive under harsh conditions, such as extreme temperatures, alkaline or acidic conditions and low oxygen availability. *Bacillus sp.* and *Staphylococcus sp*. found in the canal sediments can bind PHEs, as outlined by Wang and Chen (2008), who found that the two species immobilised Pb, Cd, Cu, Ni and Cr. Wang and Chen (2008) reported on the effectiveness of using bacteria as a bioremediation tool, but such a strategy could be problematical in this research due to the unknown combination of bacterial activity on zeolite efficiency.

Remediation using biosorption has been undertaken by Tunali *et al.* (2006) using *Bacillus sp.* to effectively absorb Pb and Cu from aqueous solutions. Tunali *et al.* (2006) also investigated factors affecting the biosorption process, such as pH, initial metal ion concentration and contact time. Although the bacteria in the canal sediments in this research are not being used for remediation purposes, their effect on metal immobility must be taken into account when designing a remediation strategy using zeolites. The effects of bacteria on zeolite efficiency are unknown and need further research. The bacteria present in the sediments can bind PHEs and if they form organo-metallic complexes could possibly still be absorbed by the zeolites (Alloway, 1995). Moreover, the effects of the zeolites on the bacteria are also unknown and PHEs could be released from organisms if the bacteria die due to the effects of the zeolites on pH and Redox, for example. The remediation strategy efficiency will be to a certain extent affected by the type and concentration/population of the bacterial species and thus a bacterial characterisation of canal sediments needs to be further investigated.

The main aim of this research was to characterise the physical and geo-chemical properties of the dredged sediments. The third triad was not a main aim of this research, but is still an important factor to consider for future research, both in terms of characterisation and remediation.

DISCUSSION
CHAPTER 7

"Never give up, for that is just the place and time that the tide will turn" – Harriet Beecher Stowe

CHAPTER 7

DISCUSSION

7.1 OVERVIEW

Canal sediments, after dredging, undergo various chemical and physical changes before they are disposed, and this research has focused on understanding these processes to help British Waterways reduce the amount of dredged sediments sent to landfill. The various analyses used in this research (as discussed in Chapter 4) have endeavoured to clarify the physical and geochemical properties of the canal sediments and the secondary processes that operate in the sediments after they are dredged and before disposal or potential remediation. The results and interpretations, presented in Chapter 5, give an overview of processes occurring in the sediments once they are dredged.

Canal sediments are spatially variable and present different geochemical properties over relatively short distances. Thus, any particular site on the canal can reveal significant geochemical and physical variations, so that individual samples are potentially heterogeneous. As a result, any remediation strategy is difficult, unless an overview of the chemical properties is taken into consideration to produce the most efficient remediation outcomes. The characterisation methodology of this research has been designed to investigate the various physical and chemical properties of the sediments that could affect the mobility of PHEs after dredging, which is of prime importance when considering remediation operations.

Research presented here is the first attempt to characterise the processes occurring in canal sediments and the metal associations in freshwater canal sediments following dredging and as part of a potential remediation strategy. Previous research on freshwater sediments (Buykx *et al.*, 2000; Doig and Liber, 2006; Large *et al.*, 2001; Naylor *et al.*, 2006; Sainz *et al.*, 2004) and the associations of metals in existing dredged disposal sites (Large *et al.*, 2001; Taylor and Boult, 2007; Stephens *et al.*, 2001a; Singh *et al.*, 2006) has focused on drying and oxidation of canal sediments as part of a disposal strategy, rather than remediation. This research has attempted to quantify the PHEs in the sediments using a combination of sequential extraction and other physico-chemical methods, such as ICP and IC for pore water, XRF and XRD for sediment chemistry, LOI and GC-MS for organic components, pH and Redox measurements for electrochemical properties, and particle size for physical properties.

7.2 GENERAL CHARACTERISTICS OF THE SYSTEM (SEDIMENT TANK)

Since canal sediments can exhibit different chemical and physical properties even at the same sites, 10 boxes filled with 9 litres of wet sediments were taken from each site to limit these variations. Initial investigation of pH and Redox was undertaken once the sediment settled in the tank, 2 weeks after dredging. The colour of the sediments did not change, except for the surface where a very thin film, approximately 2-3 mm thick, developed due to the oxidation of the sediments in contact with oxygen. The oxidation layer was limited in extent due to the compaction of the sediments which limited oxygen availability between the top sample point and the bottom sample point. This was further demonstrated by the pH and Redox analyses, as demonstrated in Section 5.1. The mean and median values were coincidental which suggests a normal distribution in the lower section of the tanks. The mean and median values in the upper section of the tank do not coincide and suggest a non-normal distribution and thus external factors such as oxidation in this case, which could have changed the distribution.

7.3 pH AND REDOX

The pH and Redox values showed that there was a clear relationship between the two, as shown in Section 5.11.1. Although Belper Bridge, Titford and Horseley Fields Bridge have different pH-Redox signatures, Pearson correlation coefficients (r) statistical analysis showed that they are correlated, with Horseley Fields Bridge and Titford having similar trends compared to Belper Bridge (Figure 46). This could be due to the longer settling time for Belper Bridge compared to the other two sites. On the other hand, since Redox measurements at Belper Bridge were all in the negative spectrum and so residence time may not have an effect at all, which would be an important factor when considering remediation. Particle size at the different sites was similar in composition and thus would not affect the pH-Redox relationship. pH-Redox values affect the mobility and accessibility of pollutants in the sediments (Chuan *et al.*, 1996; Caplat *et al.*, 2005; Förstner *et al.*, 1989; Forstner and Calmano, 1998; Gambrell *et al.*, 1991; Kelderman and Osman, 2007), but minimal research has been completed on the effect of pollutants on pH and Redox, for example, by anthropogenic inputs or where specific minerals are present. Two boxes from Belper Bridge have lower mean pH values compared to the other boxes and this could also affect the correlation between the pH and Redox correlation using ANOVA.

Another important factor to consider, especially when discussing pH and Redox associations, is the biological activity in the sediments. This research has concentrated on two of the

characterisation triad, the physical and chemical aspects of the canal sediments but not the biological aspects. Preliminary research on microbiological activity has been attempted for interest and presented in Chapter 6. pH for example can be lowered when sulphides are oxidised to sulphates by microbial activity (Lors *et al*., 2004).

7.4 PHYSICAL CHARACTERISTICS: PARTICLE SIZE

The particle size distribution for all three sites consisted mainly of the fine particles (silt and clay) than sand, with the average particle size composition of 6%, 63% and 29% for Belper Bridge, 6%, 50% and 30% for Titford and 6%, 57% and 35% for Horseley Fields Bridge for the clay, silt and sand fractions, respectively, as shown in Section 5.8. Although the different proportions of clay, silt and sand seem to be roughly the same for the three sites, statistical analysis (Section 5.11.2) showed that the particle size is significantly different between sites, which means that particle size analysis should be taken into consideration when designing a remediation strategy so as to ensure maximum efficiency of the clinoptilolite.

The preliminary particle size analysis using a Malvern Mastersizer granulometer showed that the results of the particle size of canal sediments can be skewed by two factors, namely organic matter and aggregation of clay size particles. The results showed a considerable difference before and after pretreatment and thus demonstrate the importance of effective pretreatment (discussed in Section 4.7.1) when analysing canal sediments.

Aggregation of the sediments means that more organic matter, and consequently more PHEs, can be present and stored in the sediments. Moreover, clays possess low permeability rates, decreasing more so as the sediments settle and particles are closely packed. This may explain why sediments in the sampling boxes remain anoxic, even after prolonged settling times. The water is forced upwards as the sediment particles settle and form the supernatant layer of water on top of the sediments in the tanks. Based on particle size, the three sites show similar characteristics with the same range of clay, silt and sand. Similar sediment textures were found in the Woolston Canal, Warrington, UK, with 5.5%, 65% and 29% of clay, silt and sand, respectively (Hartley and Dickinson, 2010) which is very close to the percentages found in the three sites under investigation all found in the Birmingham Canal Navigations. The texture is slightly different in the Gent-Terneuzen Canal in Belgium, with more clay than the UK canals with 36% clay, 34% silt and 30% sand. This is approximately the same partition between fines and sand compared to the sediments in the UK. These sediments also show similar pH (7.8)

and Redox (-314 mV) values (Maes *et al.*, 2003). Delfe Canal sediments have also been researched extensively but the sediments' texture have a different classification in The Netherlands and were divided between the <45 µm and >45 µm (Qu and Kelderman, 2001; Kelderman *et al.*, 2003). The results from the Delfe research show that the sediments were sandier in Delfe compared to the West Midlands, UK, samples.

Sediment texture has also been associated with specific PHEs and their distribution in the sediments. Copper and zinc seem to be the two main PHEs strongly associated with particle size distribution as shown in Table 16 (Section 5.11.3). The distribution of these elements and the particle size distribution are strongly correlated for copper and zinc and also to a lesser extent for lead for all three particle sizes. Copper has been found to be strongly associated with the particles size fraction <2 µm, which is the clay fraction (Besnard *et al.*, 2001). Zinc is also associated with phyllosilicates, due to isomorphic substitution and by specific chemical binding to hydroxyl edge sites. At higher pH, >6.5, zinc can be incorporated into neo-formed precipitates, such as iron oxides, which can form at the surface of phyllosilicate mineral and form as a coating on clay minerals (Nachtegaal and Sparks, 2004), which explains zinc's association with the different particle sizes.

The particle size will also affect the remediation strategy. Since most of the sediments are fines, the remediation strategy discussed in Chapter 6.10 would be more efficient. The sediments would be separated and kept in circulation and the remediation strategy adapted to fit the time between circulation and settling in which time the zeolites would absorb the PHEs which would have been stripped out of the sediments.

7.5 ORGANIC FRACTIONS: LOSS ON IGNITION & POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Organic carbon in the sediments analysed using organic loss on ignition were similar to other canal environments, especially in the UK (Hartley and Dickinson, 2010) with results around 30%. The dichromate method of titration was inconclusive as the colour change was too subtle, close to the end point and thus results would not have been accurate. Moreover, the waste produced contains strong acids and Cr and thus was replaced by the Loss On Ignition method, as it was not practical or environmentally friendly to repeat experiments using the titration method, as pointed out by Abella and Zimmer (2007). Moreover, LOI was the preferred method for determining organic content in sediments in this research, as LOI and Soil Organic

Carbon (SOC) are correlated with high correlation coefficients, as outlined by Konen *et al.* (2002).

The GC-MS results identified by the two laboratories were different both in identity and concentration. SAL laboratories only analysed a specific range of PAH, whereas DMU analysed the whole spectrum of PAH present in the sediments. Although concentrations were also in the report, the main aim of the analysis was to characterise the range of PAH present in the sediments. Ethyl acetate and hexane were used to extract both polar and non-polar PAHs. Although necessary measures were taken to maximise extraction (longer cycles and low heat), the more volatile PAHs would have been evaporated in the early stage of the soxthlet extraction and thus could not be characterised.

The sequential extraction results show that Cd, Cr, As and Ni were associated with the organic phase of the sediment. The organic phase does not seem to be present in all samples during the sequential extraction. This is most probably due to the organic matter surfaces becoming structurally less complex as the sediments dry, as demonstrated by Gambrell *et al.* (1991) who also observed that metals associated with organic matter can be released and re-associated with Fe/Mn oxides. Metal adsorption onto organic matter is also reduced after sulphides are oxidised to sulphates (Sposito, 1984), which is concurrent with the sequential extraction and IC results. The organic matter in the canal sediments were most probably humic acids, which are important electron sinks for anaerobic bacteria (by stimulating the mineralisation of complex organic carbon in anoxic environments) as pointed out by Lovley *et al.* (1996). Moreover, PAHs such as pyrene and benzo(a)pyrene, as found in the canal sediments, are often associated with humic sedimentary organic matter (Poerschmann *et al.*, 2007). Sediment organic matter plays an important role as electron acceptors for microbial respiration and in the mineralisation process in these anoxic sediments (Giani *et al.*, 2010). The humic substances and bacteria present in the sediments can also contribute to organic complexation of PHEs into their methyl forms. The preliminary bacterial analysis in this research identified six main bacterial species which are anoxic species, but the literature is very limited on their roles in canal sediments and whether they are sulphur reducing bacteria. Moreover, their effects on PAH is also unknown.

From the PAH results, it can be deduced that the canal sediments in the BCN area contain most of the most dangerous PAHs (Agency for Toxic Substances and Disease Registry, 1995;

Environment Agency and Chartered Institute of Environmental Health, 2008), that are also on the priority hazardous substances list under the Surface Water and Pollution Prevention and Control Regulations and Water Framework Directive (Environment Agency, 2010; European Parliament, 2008).

There has been extensive research on degradation of PAHs by bacteria (McNally *et al.*, 1999; Dean-Ross *et al.*, 2002) or algae (Ke *et al.*, 2010), but algae are effective only with low molecular weights or less than five or six aromatic rings (Ferrarese *et al.*, 2008). From the PAH identification, it can be deduced that biological remediation might not be the most effective way to remediate PAHs from the canal sediments. Clinoptilolite, which is the proposed remediation tool in this research, has been used to remediate PAHs before but was not very efficient. The clinoptilolite was modified to surfactant modified zeolites (SMZ) which increased its efficiency to more than 50% removal of PAH (Hossein and Hossein, 2007).

7.6 PHEs DISTRIBUTION IN PORE WATER

The concentrations of PHEs in the pore water were relatively low compared to their total concentration in the sediments. This was consistent with results from other research (Kelderman and Osman, 2007) on canal sediments where the PHE concentrations were lower. This was due to the anoxic conditions prevailing in the sediments and thus the high concentration of sulphides which would precipitate these PHEs. The redox potential was very anoxic in the tanks, even in the top layers, and the pH remained neutral to alkaline, which suggest that the sulphides did not oxidise to sulphates which would normally decrease the pH. The IC results showed high concentrations of sulphate for the three sites. Sulphides were below detectable limits. Moreover, since most sulphides are insoluble, it can be deduced that the sulphate concentrations in the ICP results were high due to sulphides being oxidised during sample preparation, especially centrifugation. The oxidation of the sulphides to sulphates would decrease the pH which would consequently release the PHEs associated with them. The concentration of PHEs detected by ICP was, however, lower than anticipated which could be due to PHEs being immobilised by the Fe/Mn oxides in the sediments during centrifugation. Availability of some of the PHEs associated with the sulphides may decrease, as their corresponding oxides might be less soluble. The pH of the sediments after the oxidation of the sulphides might decrease, as shown on the example below:

$$FeS_2 + 7.5O_2 + H_2O \Rightarrow 2Fe^{+3} + 4SO_4{}^{2-} + 2H^+$$

Equation 3: Sulphide oxidation and its effect on pH.

Sulphate to sulphide ratio has often been researched and it has been shown that the ratio decreases rapidly after dredging and sulphides are oxidised to sulphates within 5 weeks after dredging (Stephens *et al.*, 2001a; Stephens *et al.*, 2001b). As sulphides are oxidised to sulphates, there is a release of metals associated with them, which are subsequently redistributed into other phases in the sediments, such as hydroxides, carbonates and inclusion into the clays (Lions *et al.*, 2007) which would have occurred during the centrifugation process during sample preparation.

ICP results also showed higher concentrations of sulphur in the supernatant and top sample points compared to middle and bottom sample points. The results show that the sediments are not chemically homogenous and oxidise at different rates due to the sediments being compacted and with low rates of permeability. The results also show that the sulphide oxidation already occurs before centrifugation for the supernatant and top sample point and the level of oxidation during sample preparation is considerably smaller for the middle and bottom sample points.

Other PHEs, such as Zn, As, Sn, Sr and Pb, also follow the same pattern with higher concentration in the supernatant compared to the sediment sample points. The effect was only seen in the Belper Bridge samples. The same PHEs in the Titford and Horseley Fields Bridge samples had a more uniform distribution across the different sample points. Belper Bridge samples were kept for 2-3 weeks longer before analysis compared to the other two sites and thus the sulphides in Belper Bridge samples oxidised in the top sample point of the sediment and moved to the supernatant. The uniform distribution of the other PHEs is due to the equal oxidation time for the other samples in the centrifuge.

PHEs such as Cu, Cd and Cr were below detectable limits (0.1 µg/l) for ICP analysis for most samples. Cu and Cr were mainly associated with Fe/Mn oxides in the solid phase and consequently would not be detected by the ICP. Cadmium, on the other hand, was associated with either the pore water or exchangeable fractions. Cadmium is more mobile under low pH conditions (as would be expected when using *Aqua Regia*) than other elements in these

sediments which correlates to other research on cadmium availability by Chen *et al.* (2000), Pénilla *et al.* (2005) and Liu *et al.* (2009).

7.7 PHEs DISTRIBUTION IN SEDIMENTS

PHEs in the sediments are distributed between the solid phase in the sediment matrix and liquid phase in the pore water. The seven main PHEs considered in this research were Cd, Cu, Cr, Pb, Zn, Ni and As. The concentration of each PHE was determined using various analyses, as demonstrated in Chapter 5. The 7 PHEs had different associations in the sediments at different sites and at different sample points within the sediment boxes.

7.7.1 Sequential extraction results

The sequential extraction results were interpreted using the CISED software developed by BGS. This new method, unlike conventional methods, determines associations in the sediments and not necessarily the five fractions following Tessier's method (Gonzalez *et al.*, 2000; Tessier *et al.*, 1979). The CISED method is thus more accurate for canal sediments, but had limitations. The main issue with the CISED method was the interpretation of the different associations with regards to conventional fractions, such as organics, carbonates, oxides and exchangeable fractions. Since the CISED output is in the form of components or major associations, the corresponding fractions were derived mainly from literature and the BGS database based on the other soil types analysed using the CISED method. Alternatively, the CISED method is relatively simple using only one reagent and the short reaction time between the sample and reagent prevents remobilisation of PHEs to other fractions. Some of the components were unidentified due to lack of precedence and literature. The components are mainly made up of P, K, Zn and Mg, which suggests either an exchangeable fraction or a phosphate. The findings corroborate other research regarding phosphates in anoxic sediments. In the presence of calcium carbonate and anoxic conditions, phosphates are adsorbed strongly on calcium carbonate, which is the reason why calcium carbonate rich sediments contain low concentrations of dissolved phosphates (Gomez *et al.*, 1999) in pore waters. It also explains the IC results where phosphates were below detectable limits. Zn has a major role to play in the anoxic canal sediments. Zn is mainly associated with S and in the unidentified components with P, K , Ca and Mg. Yu *et al.* (2001) found similar results with Zn being associated mainly with Fe/Mn oxides, which could be ascribed to the high stability constants of Zn-(Fe+Mn) binding forms. Kelderman and Osman (2007), used a modified Tessier sequential extraction procedure with five fractions: exchangeable, carbonates, Fe/Mn oxides, sulphides+organic

matter and residual. The main issue with the sequential extraction is the methodology, which is quite complex and time consuming which allows for readsorption of PHEs to other fractions, thus giving an inaccurate result. Also, fraction 4 is a mix of sulphide and organics, which is confusing especially since the samples are canal sediments, where both organics and sulphides play an important part.

The components derived from the CISED software were assigned an equivalent conventional Tessier fraction. Component 1 (Figure 20) relates to the soluble PHEs in the pore water. This component is highly mobile as it is extracted in the very early stages of the extraction with deionised water. It is composed predominantly of S and Na which are likely to be derived from pore-water salts in the sediments. Component 2 can be exchangeable or organic. This component is extracted in three distinct peaks across the whole of the extraction. The presence of K and Mg indicates that the component may have a contribution from elements that are considered to be exchangeable (Rowell, 1994). However, since this component has three distinct peaks and contains K, P and S, it could be humic (organic) which is soluble in the water phase and starts to be broken down by the addition of hydrogen peroxide (steps 7 onwards) and is finally released from iron oxides at higher acid strengths (extraction 12-14). In addition, there may also be a carbonate contribution to this component, as the Ca is released at low acid strengths and at high concentration. Component 3 is a carbonate with a distinct peak with the addition of 0.01M *Aqua Regia*. This component is dominated by the presence of Ca, c.70% and likely to be derived from the dissolution of calcium carbonate, although it has a small contribution (<10%) from both Mg and Mn, which could also be carbonates or associated with the main Ca carbonate component. Component 4 has been tentatively identified as Ca-Zn sulphate, because of the dominance of Zn (c.35%), Ca (c.30%) and S (c.20%). This component is not a sulphide, as it is removed too early from the system by too low acid strengths. This component has a clear and narrow window of extraction, by medium acid strengths (0.1-0.5M). Component 5 can be either a manganese oxide or mixed Mn-Ca-Zn oxide mineral assemblage. This component is extracted in a narrow window and is first seen after the addition of hydrogen peroxide, an agent known to aid dissolution of Mn. This component is extracted at a later stage compared to other soil environments, but this could be due to the ‘dirty’ nature of the component as seen by the presence of other elements such as Ca, Zn and Cr. Component 6 is an iron oxide possibly crystalline in nature, as it is extracted at high acid concentrations (steps 10-14) during the latter stages of the extraction and in a clear, distinct window of

extraction. This component contains c.70% Fe and is probably derived from dissolution of a crystalline Fe oxide.

7.7.2 Cadmium

Cadmium is associated with the potentially more mobile phases and the stable phases in the sediments. In all three sites, cadmium is associated with the soluble, organic, exchangeable, sulphate and oxide phases. The concentrations of Cd varied widely between sites, with the highest at Belper Bridge compared to Titford and Horseley Fields. Cadmium in pore water was below detectable limits for Belper Bridge and at low concentrations (ppb) for the other two sites. These results show that Cd is leached out of the sediments with very low acid strengths, but is not present in the pore water to start with. Overall, Cd does not follow the following order, Mn oxides> Fe-amorphous> monmorillonite> Fe-crystalline= illite=humics> kaolinite> silica (Fergusson, 1990). In these sediments, most of the extractable Cd is mainly associated with components 2 and 5 which are the exchangeable/organic fractions, as observed by Christensen and Christensen (2000) and manganese oxide as observed by Turner *et al.* (2008) and also associated to a lesser extent to components 1, 3 and 6. Moreover, cadmium partitioning between the solid and liquid phase is often affected by pH, presence of other cations and organic functional groups (Lin *et al.*, 1998). The first three components requiring lower acid strength or only de-ionised water means that elements associated with them are more mobile and potentially bioavailable. The more mobile Cd is probably Cd being dissolved from sulphides. Soluble Cd is usually taken up by calcite at pH>7 (Carroll *et al.*, 1998), but since the canal sediments are at near neutral pH, soluble Cd is most probably reassociated with the more stable phases, such as the oxides for example. Cd can displace Fe in Mackinawite (Fe-Ni sulphide mineral), for example, forming (Cd,Fe)S on the surface followed by further adsorption on the surface of the transformed mineral (Coles *et al.*, 2000). Cadmium is more mobile than other elements in these sediments, which correlate to other research on cadmium availability by Chen *et al.* (2000), Pénilla *et al.* (2005) and Liu *et al.* (2009). Total cadmium concentrations in the sediments were different between sites, with the highest at Belper Bridge (100 mg/kg) compared to the other two sites with less than 20 mg/kg. These correlate with results found from the Bejei canal, Romania (Dalmacija *et al.*, 2006), where values were between 0.88 and 66 mg/kg. According to Dutch Regulations, these would be above intervention concentrations (12 mg/kg) which would mean that Belper Bridge would be above intervention concentration for cadmium (Dalmacija *et al.*, 2006). In cases where the sediments

are highly anoxic and thus have high concentrations of free sulphides, 10^{-3} M , bisulphides and polysulphides complexes may result in the sediments acting as a source of cadmium (Davies-Colley *et al.*, 1985). The bioavailable cadmium, although toxic, can be remediated by different media such as zeolites and activated carbon which has been reported to spontaneously adsorb cadmium in remediation experiments (Huang *et al.*, 2007). The remediation tool proposed in this research is clinoptilolite, which can absorb mobile Cd.

7.7.3 Copper

Copper is mainly associated with Fe and Mn oxides and thus is not bioavailable. The total copper concentrations in the sediments were higher at Belper Bridge (ca 6000 mg/kg) compared to the other two sites, Titford and Horseley Fields Bridge, which had concentrations in the region of 900-1200 mg/kg. The copper concentration in the pore water was below detectable limits, as expected. Overall, Cu in the sediments was not bioaccessible and thus would not pose any risks, even at Belper Bridge. Copper is mainly associated with components 5 and 6 which are the Fe and Mn oxides phases and to a lesser extent to component 3, which is the carbonate fraction. Cu has been found to be adsorbed onto Fe oxides and Mn oxides easier in the presence of sulphates (Pénilla *et al.*, 2005). Copper bioavailability increases with decreasing pH or increasing organic content (Gupta and Aten, 1993; Brun *et al.*, 1998). Canal sediments at the three sites are at near neutral pH, which would limit bioavailability but have high organic content (30%). Copper has been found to be associated with particulate organic matter, the more labile form of organic matter in other research (Besnard *et al.*, 2001), which would make the copper more available if the organic matter decomposed. The soil under investigation in their research was oxic and with low concentrations of Fe and Mn oxides and sulphates/sulphides which would explain the association with the organic phase. The research also found similar results in terms of particle size fractionation where copper was highly associated with the different size fractions and mainly the clay fraction, as discussed in Chapter 7.4. Chen *et al.* (2003) also found similar results with copper being associated with organic matter and phosphorus and demonstrated the leaching behaviour of copper which was in low concentrations (15 µg/l), which correlates to results found in this research for copper concentrations in pore water. Copper in pore water was not shown in the Results chapter as copper concentrations were below detectable limit for most boxes. Other research (Hamed, 2005) found that dissolved copper concentration was higher compared to particulate copper in the Suez canal area, but this was due to point source anthropogenic pollution in one of the two

sites under investigation. Copper in anoxic sediments occurs as discrete sulphides and tend to nucleate on surfaces, with a composition close to chalcopyrite (Large *et al.*, 2001) and the sediments are close in composition to the ones under investigation in the BCN. Petrography of these sulphide minerals were achieved using cryogenic SEM which could not be achieved in this research.

7.7.4 Chromium

Chromium was mainly associated with manganese oxide and iron oxide and thus was not mainly bioavailable. A lower percentage of the extractable Cr was associated with the potentially more mobile phases which could be a potential hazard, especially since more mobile chromium is usually in the form of Cr(III). The total concentration of Cr in the sediments were around 600 mg/kg for Belper Bridge and less than 200 mg/kg for the other two sites and thus the bioavailable concentration would be potentially around 30 mg/kg and thus would need to be considered in the remediation strategy. Chromium is mainly associated with component 5 which is manganese oxide and to a lower extent to components 1, 2 and 4 which makes up to ca <15% of the total extractable chromium. Cr(III) is often associated and oxidised to Cr(VI) in sediments (Sethunathan *et al.*, 2005; Rai *et al.*, 1989) but since the chromium extracted is mainly associated with manganese oxide and not with the more mobile components, it can be deduced that the chromium present in the sediments is actually in the form of Cr(III) (Bhattacharya *et al.*, 2002). Cr(VI) is more toxic than Cr(III) and assuming that the 200 mg/kg Cr is in the form of Cr(III), the risk to human health would be limited, although some research suggest that prolonged exposure to Cr(III) can cause skin allergies and cancer in humans (Yun *et al.*, 2001). In addition, Cr in these sediments are associated with manganese oxides and the presence of bacteria in the sediments might oxidise the Cr(III) to Cr(VI) under certain conditions (Sethunathan *et al.*, 2005). Although Cr (VI) is more soluble, it is often adsorbed by Fe oxides or barium sulphate (Rai *et al.*, 1989) and since Cr in the sediments are associated with one or more components, it is difficult to determine which Cr species is present in canal sediments. Other experiments with Cr(III) in anoxic sediments also showed no oxidation to Cr(VI) when reacted with seawater and the Cr(III) posed no problem, as it was mainly associated with the oxides, carbonates and phosphates which are the more stables phases (Carroll *et al.*, 2002). Remediation of Cr from contaminated sediments has been undertaken using different materials, for example clinoptilolite and agro-waste material (straw and bagasse). The latter was a more complex remediation procedure with different steps to

ensure that the adsorption kinetics were efficient (Garcia-Reyes and Rangel-Mendez, 2010). Mobile chromium from the clinoptilolite experiments decreased by 64% and the total metal amounts after 9% addition to the sludge was around 25% (Sprynskyy *et al.*, 2007). Although this research also explores clinoptilolite as a remediation tool, the clinoptilolite in this case would be in powder form (compared to rocks), which would increase the surface area and efficiency of the clinoptilolite for adsorption of Cr. Remediation can, however, be hindered by Cr(VI) which can form anionic complexes with other metals, such as Pb and Cd and decrease their removal efficiencies by clinoptilolite (Vaca Mier *et al.*, 2001).

7.7.5 Lead

Lead in the sediments was mostly associated with the iron and manganese oxides and thus were not bioavailable. Lead concentrations were not significantly different between the sites with concentrations around 800 to 1500 mg/kg for the three sites. Lead concentration in the sediment pore water was lower with concentrations below 1 mg/l, as expected, as most of the lead extractable was associated with the more stable fractions. Lead is associated mainly with components 5 and 6, which are the manganese and iron oxides, respectively. The association of Pb with these two components means that high acid strengths are needed to extract lead and thus it is not bioavailable. This is congruent with results found by McKenzie (1980), Robinson (1981) and (Tessier *et al.*, 1996). The pH at Belper Bridge, Titford and Horseley Fields Bridge was near neutral to slightly alkaline and other research on Pb for sites at near neutral pH have found that adsorbed Pb accounts for 50% of total lead and in lower pH. Pb bearing jarosites (hydrous potassium and iron sulphate) accounted for the majority of Pb (Ostergren *et al.*, 1999). Pb was mainly associated with Mn oxides which correlates with research on lead associations with Mn/Fe oxides, which showed that Pb was adsorbed 40 times more by Mn oxides compared to Fe oxides (McKenzie, 1980). Moreover, Pb was adsorbed more strongly than the other ions studied by most of the oxides, except for goethite (McKenzie, 1980). Goethite was not detected by XRD or had very low match scores and the only Pb mineral found with the XRD analysis was tsumcorite ($PbZnFe^{2+}(AsO_4)_2.H_2O$), but with a low match score (6.24). The sequential extraction showed that Pb is mainly associated with Fe/Mn oxides, but to a lesser extent with sulphides. Lead in anoxic sediments can also be associated with iron sulphides and iron carbonate on top of the additional discrete sulphide (Maes *et al.*, 2003). Removal of Pb by powdered clinoptilolite, as will be used in this remediation strategy, is also more effective than using granular clinoptilolite, as described by Inglezakis *et al.*, (2007). Pb is

one of the preferred PHEs on the selectivity (Blanchard *et al.*, 1984; Curkovic *et al.*, 1997; Inglezakis and Grigoropoulou, 2004) series for clinoptilolite, as it does not occupy the same sites as other PHEs in the cage-like structure of clinoptilolite (Badillo-Almaraz *et al.*, 2003).

7.7.6 Zinc

Zinc is mainly associated with the sulphate followed by iron and manganese oxides, which are the more stable phases and thus not bioavailable, but also with the carbonate and sulphate fraction as expected in a highly anoxic medium. Total zinc concentrations were between 15000 to 20000 mg/kg for Belper Bridge and at lower concentrations in the other two sites with concentrations lower than 10000 mg/kg. Pore water concentrations of Zinc were lower than 0.5 mg/l. Overall zinc would not pose any problems as Zn is not bioavailable although total concentrations are elevated. Since zinc is a chalcophile, it had lower affinity for oxides and preferentially bonds with sulphides/sulphates, as evident in the sequential extraction results. The results correlate with Hayashi *et al.* (1990), who suggested that Zn-HS complexes predominate in acidic solutions, whereas Zn-HS-OH species dominate Zn speciation at alkaline pH. Zinc was found to be present in specific components associated with sulphur, which is congruent with the results found by Large *et al.* (2001) who used cryo-SEM techniques and identified the different sulphide occurrences in the sediments. Zinc is mainly associated with components 4 and 5, which are the sulphate and manganese oxide components. These two components are extracted by medium acid strength and thus are not readily available. Zinc is well known for its association with sulphides, sulphates and oxides in canal sediments (Large *et al.*, 2001; Carroll *et al.*, 2002; Naylor *et al.*, 2004; Lions *et al.*, 2007). Other research on zinc in sediments have demonstrated that zinc can become more available with ageing of the sediments and thus oxidation of sulphides, which results in PHEs being redistributed and associated to other phases which could be more available (Lions *et al.*, 2007), but Zn in the sediments was distributed in different fractions. In most cases where anoxic conditions prevail, zinc occurs mainly as a discrete zinc sulphide component, as evident in the sequential extraction results and other research on anoxic sediments (Naylor *et al.*, 2004; Tack and Verloo, 1995; Isaure *et al.*, 2002). Another possible explanation can be the sorption of Zn on Fe oxide surfaces which can bond with the FeOH groups of the oxide coatings (Nachtegaal and Sparks, 2004) or form as discrete coating of zinc particles bound to the surface (Zachara *et al.*, 1989). Zeolites have been used for the remediation of zinc (Badillo-Almaraz *et al.*, 2003; Cerjan Stefanovic *et al.*, 2007; Peric *et al.*, 2004) and especially using clinoptilolite, which was

effectively used to remove zinc from contaminated sediments by ion exchange and sorption mechanisms (Cerjan Stefanovic *et al.*, 2007; Stylianou *et al.*, 2007), but in the case of the canal sediments, Zn has to be dissociated from the more stable phases before it can effectively be removed by clinoptilolite.

7.7.7 Nickel

Nickel was mainly associated with the mobile phases, the residual, carbonate, exchangeable, sulphate and at lower concentrations bound to the more stable phases, the Fe and Mn oxide. Although they were more mobile, the total Ni concentrations were lower compared to other PHEs and varied between sites, with the highest concentrations at Belper Bridge (400 mg/kg) followed by Horseley Fields Bridge and Titford with concentrations lower than 200 mg/kg for both sites. Nickel concentrations in pore water was lower than 1 mg/l for all three sites and suggests that although Ni is not present in the pore water, Ni is still bioavailable when deionised water and low concentrations of acids are added to the sediments. This difference in results could be due to the pH and Redox change between the pore water analysis and the sequential extraction procedure. Nickel is mainly associated with sulphides as NiS, but the residual phase found in those sediments could be due to soluble species of Ni bisulphide complexes and the possible competition of Fe^{2+} with Ni^{2+} for binding sites on organic matter (Doig and Liber, 2006). Nickel has been mostly associated with iron and manganese oxides in soils (Sastre *et al.*, 2001; Sadiq and Enfield, 1984) compared to the anoxic sediments under investigation. Nickel has been removed effectively with treated pulverised fuel ash, which is another potential remediation tool in this research. The effectiveness of the PFA was between 30 and 90% depending on the initial concentration of nickel (Wang *et al.*, 2006). Manganese oxide dissolution has been found to be a main source of Ni in harbour dredged sediments (Naylor *et al.*, 2004) compared to the results found in this research and other contaminated sediments, where Ni was found to be mostly in the mobile phases (Prica *et al.*, 2010).

7.7.8 Arsenic

Arsenic is associated with both the mobile and non-mobile phases in the sediments. It is well known that As is associated with Fe and Ca, which explains its association with the carbonate and iron oxide fractions. Arsenic associated with the mobile phases is lower than the concentration associated with the stable fractions and thus most of the As is not bioavailable. Total As concentrations in the sediments were around 100 mg/kg for Belper Bridge and around 50 mg/kg for the other two sites. Arsenic levels in pore water were very low at all three sites.

The varying mobility of As at different levels in the sediments has also been evident in other research where As levels in pore water varied with depth, especially where Fe/Al were in lower concentrations, which may have contributed to the solubility of As, but a lack of comparable data makes the recorded concentration in pore water difficult to interpret (Clemente *et al.*, 2008). Moreover, As does not follow the same behaviour as the other PHEs, especially the amphoteric elements as evident in various experiments (Gardner *et al.*, 2007; Moutsatsou *et al.*, 2003; Sadiq *et al.*, 2003). The use of the new sequential extraction method showed the different associations of As in the sediments and thus the results were more precise compared to the Tessier's scheme, which can overestimate the concentration of residual As (Gleyzes *et al.*, 2001).

7.8 PHE DISTRIBUTION BETWEEN SAMPLE POINTS

The tank replicates, although containing sediments from the same site, were analysed based on three virtual layers (sample points), top, middle and bottom. These were not defined by any markers apart from the distance from the oxidising layers and since the tanks were filled up to 12 cm, the three layers were made up of four centimetres of sediments each. Since other research on canal sediments were mostly *in situ* (Kelderman *et al.*, 2003) or were analysed using different setups, the hypothesis that the sediments would behave differently in the same tank had to be verified. The results for the main PHE distribution in the sediments in terms of their total concentration were analysed using 2-way ANOVA to assess the difference in terms of sample points. The seven PHEs under consideration, Cr, Cu, Cd, Pb, Zn, As and Ni showed that there was no significant difference ($P>0.05$) between sample points, except for Pb (very significant) and Zn (significant). The Bonferroni *post hoc* test showed that the mean top sample point concentration of zinc was significantly different from the other two sample points at Belper and not the other two sites. However, the middle and bottom sample points were not significantly different from each other. Lead follows the same pattern as Zn and this could be due to the mobilisation of Pb and Zn during resuspension in the tanks after dredging, which were then re-adsorbed into the iron sulphides and other metal sulphides (Maddock *et al.*, 2007). Trace metals are often adsorbed onto iron sulphide minerals or coprecipitate with them (Simpson *et al.*, 1998; Morse and Luther, 1999). Zinc and Pb also form metal sulphides prior to iron pyrite in anoxic sediments as from a thermodynamics point of view, trace metal sulphides will form first due to their low stability constants after resuspension (Buykx *et al.*, 2000). This occurred in Belper Bridge only as the concentrations of PHEs in Belper Bridge were higher

compared to the other sites based on the sequential extraction data. The higher concentrations of Pb and Zn in the top sample point compared to the other two sample points could also be due to the sulphidic transformation in the anoxic zone of heavily polluted sediments. This can consequently lead to the genesis of discrete phases which is restricted to the immediate surroundings of the original site where the metals (as macroscopic metal wastes or small metal or metal oxide particles) are supplied to the sediments (Zaggia and Zonta, 1997). Overall, since the concentrations of the main PHEs were not considered significantly different between the sample points, it can be concluded that the box replicates would be considered as one entity when the remediation strategy is implemented.

7.9 INTERPRETATION OF PROCESSES

Canal sediments are rich in organic matter as a result of high input of leaf litter and debris from the banks and vegetation growing in the canals. Moreover, there are anthropogenic organic compounds which enter the canals through surface runoff of pesticides and herbicides (for example). The organic matter in the sediments control metal mobility through processes such as chelation, which is the formation of complex soluble molecules with certain metal ions, inactivating the ions so that they cannot react with other elements. It is unclear at this stage how much the organic fraction in the sediment affect the mobility of the sediments, but from the sequential extraction results, the organic associations were not as distinct as expected. SEM-EDX data shows that the sediments are often coated by organic matter as the carbon percentage is higher than other elements in all samples analysed. Since the PHEs in the sediments are strongly associated to sulphides/sulphates and Fe/Mn oxides, the organic matter is most probably associated with these components. Secondary processes after dredging also involve to a certain extent oxidation of phases like sulphides, resulting in the release of PHEs but which are reassociated with other phases, as demonstrated by the ICP results and IC results.

7.10 PHE DISTRIBUTION BETWEEN SITES

Variation between the concentrations of the PHEs in the sediments were considered extremely significant ($P<0.0001$) for all the PHEs. The results were also extremely significant for pore water elemental concentration ($P<0.0001$) and for pore water ionic concentration ($P=0.0007$). The results were considered extremely significant for Redox ($P<0.0001$) but not quite significant for pH ($P=0.054$). Since most of these parameters are significantly different between sites, it was concluded that the three sites should be considered separately in the remediation strategy and consequently any other site that would be dredged and undergo

remediation, would have to be 'fingerprinted' and characterised prior to remediation. In general, the three sites did not vary in physical characteristics such as pH and Redox, particle size and organic content, but mainly in concentration of PHEs and their associations in the sediments.

7.11 DISCUSSION OF RESEARCH AIMS

AIM 1: Geochemical and geophysical characterisation of canal sediment (form, size, oxidation state, pH, supernatant and behaviour).

An extensive literature review on PHE bioavailability and accessibility in sediments has been presented in Chapter 2. The sampling strategy was devised to investigate three different sites on the Birmingham Canal Navigations. The sampling methodology and laboratory experiments were devised to mimic the conditions after sediments are dredged from canals. The experimental setups and sampling strategy have been discussed in Chapter 3. The geochemical and geophysical characterisation were achieved using different analyses, as discussed in Chapter 3, and the results have been presented in Chapter 4.

Aim 2: To model behaviour of PHE in canal sediments and design remediation strategy accordingly.

The PHE distribution in the sediments was investigated using sequential extraction, which was supported by other proxy analyses such as XRF, XRD and SEM-EDX for sediment PHE concentration and ICP, IC for pore water analysis. The extensive data set shown in Chapter 4 clarified the bioavailability and mobility of these PHEs, facilitating the design and conceptual operation of a remediation strategy (Aim 3)

Aim 3: Develop a remediation strategy for canal sediments (and potentially other contaminated sediments) and to assess effectiveness of zeolites and PFAs for remediation of canal sediment (CSR).

An extensive literature review on remediation using zeolites has been carried out and a theoretical remediation strategy has been discussed in Chapter 6. The pilot study experimentation carried out in the laboratory showed that there was a mass balance difference for elements between the sediments and zeolites which warranted the extensive characterisation of the sediments before attempting any new remediation trials. This research

presents a new remediation strategy, based on all the evidence, data and characterisation presented in Chapter 5.

7.12 CONCLUSIONS

This work has highlighted various important considerations for canal sediments after dredging:

1. The influence of 'site' remains an important factor to consider for British Waterways as the different sites had different 'fingerprints'. Each site should be characterised and the database would help in the potential remediation of these sediments. The three sites were all in the Black Country area and although there are many similarities with other research on canal sediments (both UK and EU), there are still minor characteristics, which could affect the mobility and bioavailability of PHEs in the anoxic sediments.
2. This work has also highlighted the inappropriate use of trigger values, such as total metal concentrations or CLEA, often imposed by strict EU or UK laws. British Waterways has on several occasions raised the issue of using Environment Agency regulations regarding dredged sediments. This research further supports their contentions that PHEs in sediments may not be mobile or bioavailable and as such 'total' concentrations are of limited value. Results presented have shown that PHEs in sediments are often associated mainly with stable compounds, such as Fe/Mn oxides, and this indicates a different classification for the dredged sediments is required possibly resulting in lower costs for British Waterways.
3. The speciation proposed by regulators following the Framework for Classification of Contaminated Soils as Hazardous Waste (Environment Agency) assume the worst case speciation (in brackets) for PHEs in canal sediments:
    a. As (As_2O_5) - Soluble in water at 20 °C with a solubility of 658 g/l. This is highly unlikely to be a major constituent of canal sediments, as ICP and sequential extraction results both show that As was not associated with the mobile phase.
    b. Cd ($CdSO_4$ or $CdCl_2$) - $CdSO_4$ is highly soluble at 755 g/l, whilst $CdCl_2$ at soluble is 1400 g/L. Cd concentration were low in both ICP and sequential extraction results which suggests that Cd was not in the form of $CdSO_4$ or $CdCl_2$.
    c. Cr (CrO_3) - CrO_3 solubility is 630g/l and a powerful oxidising reagent not compatible with organic matter. Cr was also below detectable limits for ICP

analysis and therefore CrO_3 is highly unlikely to be the speciation for Cr and more likely to be associated with the stable phases, such as Fe/Mn oxides.

d. Cu ($CuSO_4$) - $CuSO_4$ has a solubility of 143 g/l and Cu was also below detectable limits for ICP results and therefore $CuSO_4$ is highly unlikely to be the speciation for Cu.

e. Pb ($PbSO_4$) - $PbSO_4$ is poorly soluble in water, 0.04 g/l, but results from sequential extraction show that lead is mainly associated with Fe/Mn oxides. Therefore $PbSO_4$ is a potential component in the sediments but Pb more likely to be in the stable phases.

f. Ni ($NiCO_3$) - Sequential extraction data shows Ni is associated with carbonates, but also with the exchangeable phase. XRD results from BW also suggest they are in the sulphide form and upon oxidation would be released and readsorbed by other phases. Therefore, Ni is potentially in the form of $NiCO_3$.

g. Zn ($ZnSO_4$) - $ZnSO_4$ is highly soluble >2000 g/l and therefore highly unlikely to be the main constituent of canal sediments. The sequential extraction data shows Zn is associated mainly with Fe/Mn oxides and S, but had low concentrations for ICP results, suggesting Zn was either in the sulphide form or bound to Fe/Mn oxides.

4. The data from this research confirms BW arguments that the main PHEs are actually in a more stable form until the sediments are dried and oxidised, followed by the release of the PHEs associated with the sulphides. Although the PHEs are mobilised in the sediments under anoxic conditions, other processes occur during drying and oxidation, as outlined by Stephens *et al.* (2001a). This research focused on characterising the dredged sediments soon after they are dredged and before any disposal decision is taken. Characterisation of the sediments meant that the PHEs can be localised between the different fractions in the sediments and thus a remediation strategy can be developed accordingly saving time and money for British Waterways (Beckwith, 2007c).

5. Many processes occurring in the sediments depend on the water content. After dredging, the high water content encourages the sediment to settle and become compacted and thus remain anoxic. The sediments once settled are still water logged and thus not oxygen permeable. This allows the bottom of the tank to remain highly

anoxic and a thin greyish layer (approx. 3mm thick), a result of oxic, aerobic conditions, to form on the surface of the sediments.

7.13 FURTHER WORK AND REMEDIATION STRATEGY

This research has successfully characterised PHEs and their associations in dredged canal sediments. The main issue with the initial experiments (pilot study) using clinoptilolite was the mass balance issue and the main question was; where are the PHEs? The new remediation strategy is derived from the characterisation part of this research and especially the sequential extraction data. From the results, it can be concluded that all the PHEs are either associated with the sulphides and the more stable phases, such as the Fe/Mn oxides. PHEs associated with the soluble phases are the easiest to remediate, as they would be in solution and thus be adsorbed by the clinoptilolite as long as they are in contact. The PHEs are also associated with sulphides which are insoluble but sulphides are oxidised to sulphates, which release PHEs associated with them. After dredging, the sulphides would oxidise as long as there is a supply of oxygen. PHEs associated with the Fe/Mn oxides are the hardest to remove, as Fe/Mn oxides are the most stable phases in the sediments requiring high acid strength to dissolve them.

The sediments at Belper Bridge, Titford and Horseley Fields Bridge have similar physical and chemical properties. All three sites have the same texture (particle size) and organic content. The sequential extraction results were also similar for the three sites and thus the same remediation strategy and design can be applied to all three sites.

7.13.1 Remediation strategy

The first option for removing PHEs from the dredged sediments is to reduce the pH of the system. The pH would naturally decrease with oxidation of sulphides to sulphates, as discussed in Section 7.6, but the pH needs to be decreased to a pH of 2-3, which would encourage mobility of PHEs. A buffer solution would be needed for lowering the pH of the sediments. The process of oxidation would start once the dredged sediments are transferred to the remediation tanks (Figure 47). A similar project was developed by British Waterways (called Aquarius) with similar aims to remove PHEs from dredged sediments (Section 2.4.1). The project was a joint project between British Waterways and Birmingham City Council established in 1992 using bentonite as a remediation tool. The main issue with Aquarius was the choice of remediation tool, as Bentonite is a cementitious material. In the case of Aquarius, the Bentonite mixed with the sediments turned into thick slurry limiting the potential efficiency

of the material. The sediments having a high water content naturally settled at the bottom of the tank and the slurry quickly absorbed all the water (bentonite being well-known for its high absorption capacity) making the remediation process difficult to operate. Plates 10 and 11 show the Aquarius Project, on a small scale and large scale basis. The project was abandoned in 1993 after small scale and large scale experiments were not as efficient as expected.

The new remediation strategy proposed in this research (Figure 47) has three main differences compared to the Aquarius Project. Firstly, Clinoptilolite is the proposed remediation tool and although it also absorbs water, the absorption capacity compared to Bentonite is lower. Secondly, the remediation tool, clinoptilolite in this case, will not be mixed with the sediments but instead enclosed in a thin membrane allowing transfer of PHEs from sediment to zeolite in an aqueous environment. Thirdly, the proposed remediation strategy includes propellers which would aid the mixing of the sediments. Mixing is important for firstly helping with the oxidation process and secondly, preventing the sediments from settling down and limiting the efficiency of the remediation tool.

The proposed remediation strategy takes into account the main issues with previous remediation endeavours. Adding Bentonite to sediments means that although the resulting material is inert, the volume of waste generated is increased. The proposed remediation strategy, however, uses Clinoptilolite in membranes which can be removed and recycled, which results in lower waste generation. Moreover, the remediated sediments can be used for agricultural purposes, making it a resource rather than a waste. Furthermore, the concentration of PHEs, such as Zn and S, are in concentrations that could be regarded as economical to recover. More research has to be undertaken on the recovery of the PHEs from Clinoptilolite once they have been adsorbed. The second important factor to consider is cost. The remediation tool, Clinoptilolite is a naturally occurring zeolite and can also be synthesised from pulverised fuel ash (PFA). PFA is a waste product from energy generation using coal. Using PFA to synthesise zeolites means waste would be reduced in another sector at a minimal cost making it sustainable. The buffer solution used in the remediation strategy to lower the pH of the system would be the only factor which would have to be reviewed before being implemented. The buffer solutions could be costly or environmentally unfriendly.

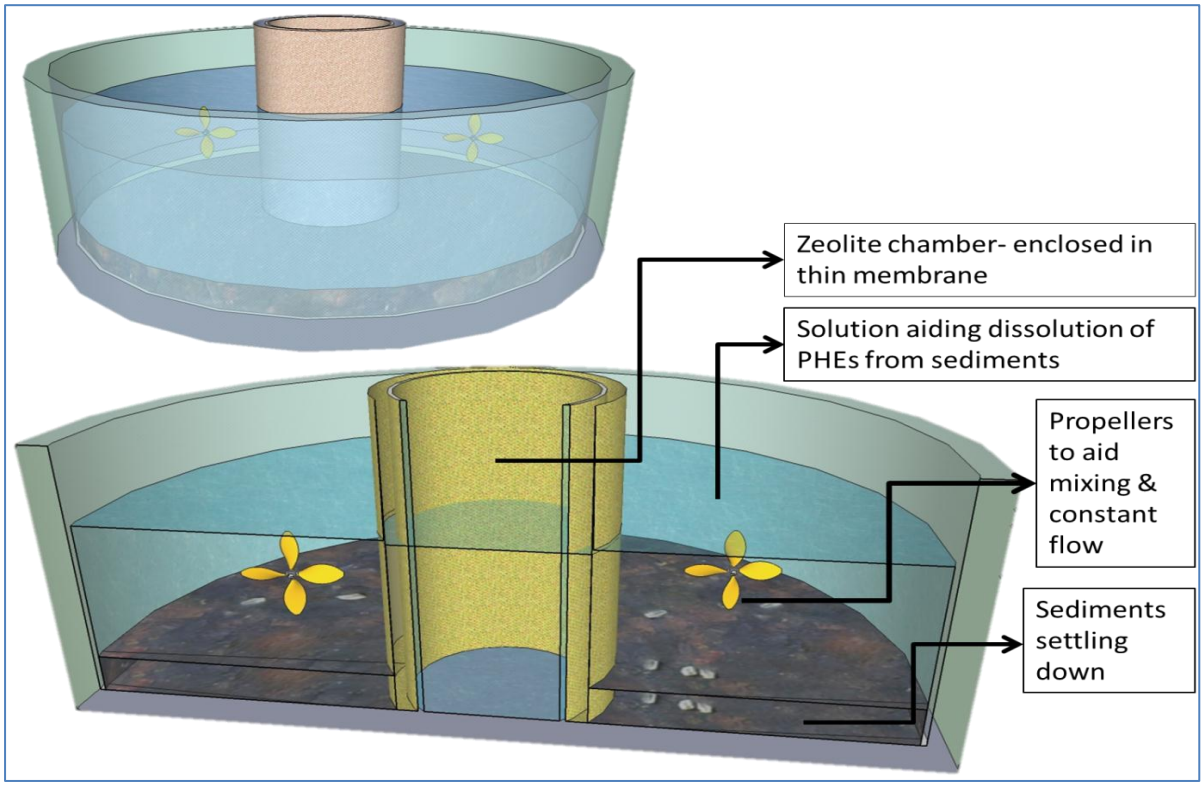


Figure 47: Remediation setup with continuous flow system showing sediment remediation tanks with zeolite core in the centre.

Plate 10: Aquarius Project showing circular tank similar to remediation strategy proposed in this research.

Plate 11: Aquarius Project on a large scale basis in Birmingham, UK.

7.13.1 Large scale remediation experimentation

The remediation experimentation shown in Figure 48 can also be used closer to sites on a larger scale, where sediments and water are pumped into a channel system. The zeolite in the system can be recycled and the sediments once remediated can be used for other purposes such as agriculture. Laboratory scale feasibility test would have to be designed first to assess the effectiveness of the system. Before achieving large scale remediation, it would be recommended that more research is conducted on the effectiveness of the zeolites to remediate the sediments. Moreover, more research is required on the waste management side in terms of end-products. The viability and new classification of the treated sediments can be a major factor to consider in terms of end-product. Moreover, the zeolites after being reused several times will lose their efficiency and would have to be treated as waste. Although the volume of zeolites would be considerably less than the volume of sediments, cost-benefit assessments would have to be undertaken before the large scale trials.

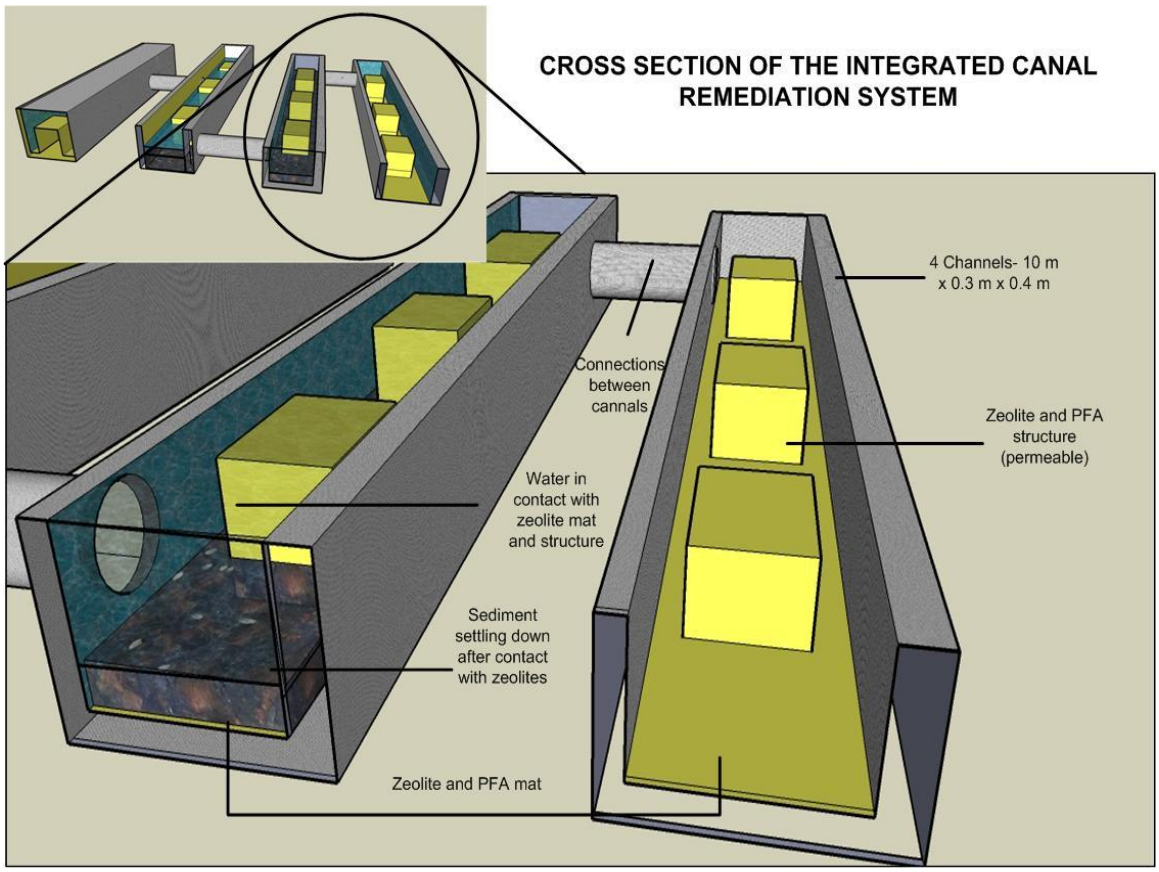


Figure 48: Large scale remediation setup with continuous flow system with canal water and sediment entering system at one end and exiting at the other and removable zeolite blocks.

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"Start by doing what is necessary, then do what is possible, and suddenly you are doing the impossible." – St. Francis of Assisi

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Appasamy, D., Roberts, C. and Williams, C. (2009b) *Characterisation of canal sediments-where and in what form are the heavy metals?* (Internal Seminar). Univeristy of Wolverhampton.

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Unpublished papers

Appasamy, D., Roberts, C. and Williams, C. (*in prep.*) Physical and Geochemical characterisation of canal sediments in the Black Country, West Midlands and their potential remediation using zeolites and PFA.

Appasamy, D., Roberts, C., Williams, C., Cave, M. and Wragg, J. (*in prep.*) Canal sediments characterisation using the CISED Sequential Extraction method.

APPENDICES

1. CONTENTS ON CD (Available from the author on request)

2. RISK ASSESSMENTS

3. BRITISH WATERWAYS INDEMNITY FOR ENTRY OVER THE BOARD'S PROPERTY

4. POSTERS

On CD:

	FOLDER:	CONTENTS:	
1.1	RAW DATA	1. THREE SITES	3. TITFORD
		2. BELPER BRIDGE	4. HORSELEY FIELDS

1.2	SEQUENTIAL EXTRACTIONS	1. H1T	11. T7B
		2. H2B	12. T7M
		3. H2M	13. T7T
		4. H2T	14. T9B
		5. H5B	15. T9M
		6. H5M	16. T9T
		7. H5T	17. SEQ ALL
		8. H8B	18. TENTATIVE ASSESSMENT
		9. H8M	19. COMPONENTS & ASSOCIATIONS GRAPHS
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1.3	SEM	1. INITIAL IMAGING DATA	2. EDX DATA (344 SAMPLES)

1.4	PARTICLE SIZE DATA	1. PARTICLE SIZE PDF REPORT-ALL SAMPLES	3. PARTICLE SIZE GRAPHS
		2. PARTICLE SIZE ANALYSIS	4. RESULTS PRIOR TO SAMPLE PREPARATION

1.5	STATISTICS	1. ELEMENTS	4. pH & REDOX
		2.ICP AND IC	5. XRF
		3. PARTICLE SIZE	

1.6	**BACTERIA (AGAR AND BACTERIA PICTURES)**
1.7	**FEASIBILITY TEST REMEDIATION RESULTS**
1.8	**GC-MS RESULTS**
1.9	**XRD INDIVIDUAL GRAPHS**
1.10	**XRD ALL (MATCH SCORE + INTENSITY)**

Risk Assessment			
Site:	Hazard:	Risks:	Control Measures:
Working in laboratory (MA 042)	❋ Working with flammable or hazardous substances ❋ Working with hot appliances (oven, incubator) ❋ Handling of equipment	❋ Risk of causing fire or risk to human health ❋ Getting seriously burnt ❋ Getting injured while handling heavy equipment	❋ COSHH forms filled in and lab-technicians gave briefing about procedure in case of fire/ fire exits and extinguishers shown. Also first aid providers near the labs known. ❋ Manual handling of most equipment for lab042 shown-XRF and ovens. Appropriate handling of materials coming out of ovens and protective gear and location shown. ❋ Disposal of waste also demonstrated.
Laboratory (MA 405	❋ Working alone on the roof ❋ Working with heavy boxes	❋ Risk of getting injured/unconscious/cold ❋ Risk of getting back injury	❋ It has been agreed that a member of the supervisory team will always be aware of the times laboratory work will be done- in this case always during office hours. Colleagues will also be aware when lab work will be performed in MA405 and can be contacted by phone if there is any emergency. Security officers will also be aware of working times.
Other laboratories	❋ Working with heavy and large equipment	❋ Risk of injury while handling equipment	❋ Necessary training has been undertaken and procedures will be supervised by member of staff (GC-MS, Ion chromatography, SEM-EDX, Mastersizer,XRF and XRD).
Sampling site	❋ Tripping and falling ❋ Working with contaminated sediments	❋ Risk of injury or drowning ❋ Health problems, infections	❋ Sampling will be supervised by member of staff (usually 2). General caution applies. ❋ Wearing appropriate clothing and protective gear (gloves, goggles)

Appropriate training has been undertaken for sample preparation and general knowledge about technique used, although most of this equipment is operated by qualified staff only. Safety procedures and hazards have also been considered and discussed with laboratory technicians. Tests involving liquids will be undertaken when staff is present in the laboratory vicinity.

INDEMNITY FOR ENTRY OVER THE BOARD'S PROPERTY

IN CONSIDERATION of your permitting entry upon the property of the British Waterways Board ("the Board") commencing on the 18th day of January 2008 and expiring on the 30th day of June 2009 located on/along the

Birmingham Canal between Wolverhampton and Birmingham for the purpose of research.

I/WE HEREBY UNDERTAKE AND AGREE, notwithstanding any supervision given or approval expressed by the Board:

1 To fully and effectually indemnify the Board, their servants and agents against:

(a) all liability whatsoever for damage to property whether owned by the Board or third parties and

(b) any other damage loss costs and expenses howsoever caused or incurred and

(c) any liability that may arise to the public or employees of the Board in respect of personal injury, death, damage or loss of property however caused

which would not have arisen but for the exercise of this permission save where the same are caused by, or arise out of, any negligent act (subject to and without prejudice to paragraph 3)

2 To insure with an office of good repute against my/our liability to the Board and a third party under paragraph 1 above and produce to the Board prior to entry on the Property a certified copy of the policy and receipt for payment of the premium or other evidence of the terms of the policy or evidence of payment for inspection whether demanded or not PROVIDED THAT if the indemnifier is self-insured it supplies the Board on request with evidence of self-insurance.

3 To obtain and comply with all safety and statutory requirements affecting our activities.

4 To be responsible for ensuring the Board's Property is suitable for the purpose we propose and to be responsible for informing any participants of any potential risks and dangers.

5 To assure ourselves of the safety of the towpath before:

(a) the event commences and make all necessary enquiries of statutory undertakers or other bodies as to whether there are any cables pipes wires or other medium which might cause any obstruction or injury whatsoever to the individuals taking part in the event.

(b) to bring to the attention of all participants of the event the dangers of waterborne diseases particularly Weil's Disease as follows:

(i) Unlike tap water, the water in canals, rivers and reservoirs is untreated and micro-organisms are naturally present. However, although the risk of contracting illness (including the much publicised but rare condition Weil's Disease) is extremely small, sensible precautions should be taken as follows:

- Avoid full immersion in the water.
- Cover all cuts and abrasions with waterproof dressings before contact with the water.
- Wash all exposed skin after contact with water and before eating.
- Do not put wet ropes, fishing lines or other objects in your mouth.

(ii) Should any illness occur within 2 weeks of contact, you should seek medical advice and inform your doctor you have been in contact with untreated water.

6 Subject to my/our Statutory rights that the Board may withdraw this permission at any time:

(a) without any liability by the Board for consequential or economic loss to the organisers, members, guests, invitees, appointed servants.

(b) in which case the Property shall immediately be vacated and any necessary re-instatement carried out at our own expense to the satisfaction of the Board.

7 Not to use the Property other than for the purpose specified above.

8 Not to permit or allow any news media (including TV companies) to report or film our activities without the Board's prior consent in writing.

10 The organisers will familiarise all participants in the event with the Board's By-laws and outline to them the "course" and in doing so point out any hazards to be encountered en route. Copies of the Board's Bye-laws can be obtained from British Waterways, Customer Services, 64 Clarendon Road, Watford, Hertfordshire, WD17 1DA, enquiries.hq@britishwaterways.co.uk.

DATED this 18th day of January 2008
SIGNATURE : C. Roberts/ D.appasamy.

NAME AND ADDRESS of organisation :MA block, city campus north, University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1LY.

CANAL SEDIMENT REMEDIATION USING ZEOLITES AND PULVERISED FUEL ASH

UNIVERSITY OF WOLVERHAMPTON
School of Applied Sciences
Dan Appasamy, Dr. C.Roberts & Prof. C. Williams
Research Centre in Applied Sciences (RCAS)
University of Wolverhampton
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Introduction

Heavy metals have been widely studied in the past in various fields of research including pedology, chemistry and pollution sciences. Unfortunately, not much research has been done on these heavy metals and their behaviour in canal sediments which are different to soil environments due to the introduction of anoxic conditions. These heavy metals behave very differently in canal sediments and characterisation is important before any effective remediation of canal sediments can be envisaged. Heavy metals can be toxic to human health and the environment at concentrations deemed unacceptable by regulations and so heavily contaminated sediments from canals have to be treated as hazardous when dredged, according to rapidly changing regulations for the European Union and in the UK, implying very high cost of transport and disposal and a solution to the problem has to be found so that important development and regeneration of canals are not hindered by other costs faced by British Waterways (Beckwith, 2007) which are responsible for miles of navigable waterways in England as shown on Figure 1.

Aim:
To remediate and stabilise sediments so that they can be disposed in normal landfills

How?
Conceptual model developed using zeolites and Pulverised fuel ash

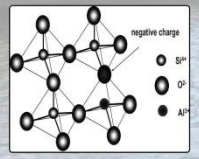
Figure 1: BCN managed by British Waterways, (author)

Canal sediments

Not widely studied except for Delfe, Netherlands
Deadline for water quality (Water Framework Directive approaching)
Research show that heavy metals move horizontally and vertically and are affected by changes in oxygen, pH and temperature (Kelderman *et al*., 1998)
Undergraduate project showed that heavy metals remain locked up in sediments for long time as long as they are not disturbed (Appasamy, 2006)

Figure 2: relict industries along the BCN- match the concentration level of samples

Zeolites



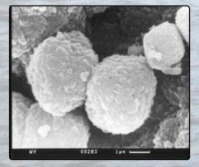


Figure 3: zeolite structure and SEM picture (Querol et al., 2002, Williams C., 2007)

Naturally occurring hydrated aluminosilicate minerals belonging to the class of minerals known as the tectosilicates.
Three dimensional structure consisting of a framework of SiO_4 and AlO_4 tetrahedra (Erdem, 2004). The aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms and the isomorphous replacement of Si_{4+} by Al_3, produces a net negative charge in the lattice as shown in the figure 3.

Net negative charge balanced by exchangeable cations such as sodium, magnesium and potassium which are in turn exchangeable by other cations such as lead, cadmium, zinc, chromium Querol *et al.*, 2002, Ouki and Kavannagh, 1997)

Exchangeable cations are harmless to the environment making zeolites appropriate for the removal of heavy metals from water and sediments (Panayotova, 2001).

Synthesis of zeolite from coal fly ash has become very attractive due to the production of zeolites with required properties and with fewer impurities (Querol *et al.*, 2002, Terzano *et al.*, 2005, Wang *et al.*, 2006).

Large scale production also means lower final cost making it one of the cheapest absorbents (Babel and Kurniawan, 2003).

Methodology and preliminary research

A preliminary research has been conducted to test the feasibility of the proposed technique for remediation of canal sediments. A sample site with highest heavy metal concentration was chosen according to results obtained from previous heavy metal provenancing research on the Birmingham Canal Navigations. The sample was taken to the laboratory and kept under anoxic conditions. Fine powdered clinoptilolite was used in pillow-case like voile mats and placed over the canal sediments in A4 size tanks. The volume ratio of clinoptilolite to sediment was 1:7 (which will be subject to change later in experimental setup) and this was left undisturbed for 7 days. Anoxic conditions were maintained by a tight sealed lid and the whole setup was covered with a black plastic bag to replicate canal conditions. Samples were taken before the experiment from the sediment and clinoptilolite. These were analysed by XRF (X-Ray Fluorescence Spectroscopy). After 7 days, the top 10 cm layer of the sediments (about ¾ of the whole sample) was homogenised and analysed again by XRF. Errors were minimised by taking 10 samples before and after experiment for both sediment and clinoptilolite.

Preliminary results

Preliminary results showed that clinoptilolite with this ratio absorbed between 6% to 40% heavy metals with 114 ppm of lead and 952 ppm of zinc. The table 1 below shows the results for more heavy metals.

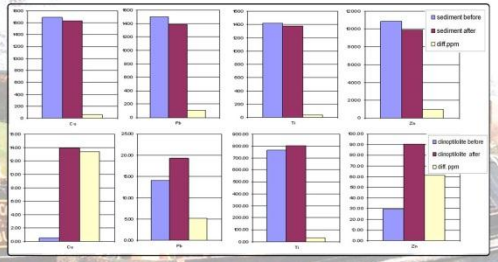


Table 1: preliminary results, heavy metal concentration decrease in sediment and increase in clinoptilolite (ppm)

Model proving

Overall the ratio used proved that the concept worked and model can now be expanded with various experimental setups as shown on the figure 4 below.
The tanks which are 255 x 395 x 155 mm (A4 size) will have a base of gravel of about 20 mm which will then be covered by about 100 mm of sediments

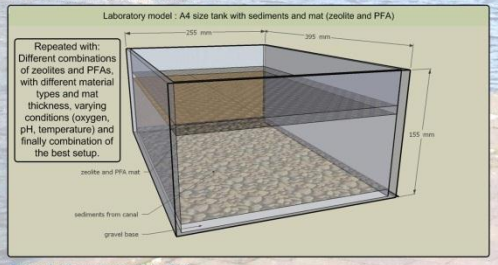


Figure 4: laboratory model (author)

There are obviously hundreds of different combinations of the laboratory setup since we are using different materials with different variable parameters but for model-proving purposes, the most effective variables according to literature will be used. All the tanks will be in triplicates to reduce errors. Since absorption by zeolites are quite quick, these setups can be repeated with different variables over the research period.

Geochemical analysis

Since heavy metals behave differently in canal sediments and with varying parameters, several techniques will be used to analyse the sediments and heavy metal concentration. Sequential extraction will be used on some of the setups together with the other techniques as shown on figure 5 below.

Figure 5: geochemical analysis

Conclusion and Way forward

Since the pilot study showed positive results, model proving and experimental setup can now be expanded with the different laboratory setups. Once the model proving is completed, the concept will be up scaled and integrated into a canalside sediment and water remediation system as shown on the figure 6 below.

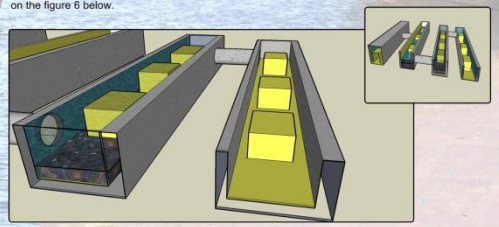


Figure 6: larger scale model of remediation system (author)

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PHYSICAL AND GEO-CHEMICAL CHARACTERISATION OF CANAL SEDIMENTS (UK) & THEIR POTENTIAL REMEDIATION USING ZEOLITES AND PULVERISED FUEL ASH

ConSoil 2010

UNIVERSITY OF WOLVERHAMPTON
School of Applied Sciences

CANALS

Important part of the industrial revolution & used for the transport of raw materials and end-products

Made redundant with improved road & rail networks.

Shifted from transportation purposes to recreational-boating, cycling, fishing, walking (Waterscape, 2009).

Major regeneration & development sites across the UK- e.g. Olympic site, BCN docks (Beckwith, 2007).

CANALS → Sedimentation → Sediments dredged for navigability purposes (Kelderman, 2000)

Sediments dredged for navigability purposes (Kelderman, 2000) → Act as sink for potentially hazardous elements (PHE)

Act as sink for potentially hazardous elements (PHE) → Wide range of PHEs depending on type of industry surrounding canals

Considered liquid & sometimes Hazardous Waste implying high disposal cost for British Waterways

Thorough characterisation needed in order to design efficient remediation strategy

SITE DESCRIPTION

3 sites in the Black Country, UK

Belper Bridge (on the Wednesbury old canal which is a connection from the Walsall, Tame valley & Wednesbury Old line canal connected to the BCN).

Titford (Known for high organic content (tar being main industry there during industrial revolution).

Horseley fields Bridge (Known for high industrial activity during the industrial revolution).

Expected high concentration of PHEs due to their historical use but with different signatures (different industries).

Dredging costs- £ 3.9m (2009/10), 2.1m (2008/09)- ↑86%
Government grants-£ 70.2m
BW expenditure- £ 192.4m

Sediments exempted from hazardous waste classification under certain conditions- can thus be reused in stabilisation work or disposed on banks/ towpaths or agricultural land. For e.g.,£ 1.5m saved in Yorkshire by reusing sediment.

Money saved on disposal can be reinjected into other restoration/regeneration projects

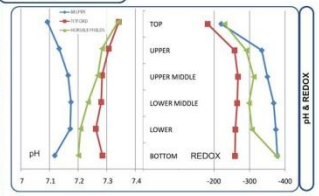
METHODOLOGY

pH and REDOX were measured in the boxes at various depths with a WVR pH-100 meter. These were replicated 5 times for each box. Ten PVC pipes were then inserted at different locations in the tanks and the tanks were frozen at -20°C. The cores were then taken out of the tank and sectioned into three (top, middle and bottom layers). These underwent X-Ray Fluorescence spectroscopy, X-Ray Diffraction, Inductively Coupled Plasma- Optical Emission Spectrometer, Ion Chromatography, GC-MS, particle size, Loss on ignition and Sequential Extraction.

The sequential extraction method (CISED), was developed by the British Geological Survey (BGS) and used various molarities of Aqua Regia to determine the various components present in the sediments and the associations of the various elements with these components. The method is time and cost effective and has various advantages over the previous methods used by researchers (Cave, 2004).

The data from the Sequential Extraction together with the various other analyses provides a good understanding of the processes going on in the sediments.

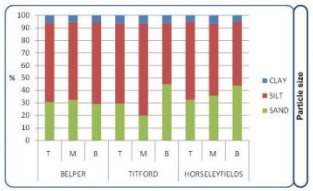
RESULTS

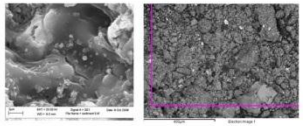


The pH values for the three sites under investigation showed that there is not much variation between the sites and with depth. The redox potential for the three sites, although in an oxygen rich environment stayed very anoxic at the bottom of the tanks increasing gradually towards the top.

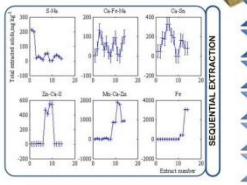
Particle size analysis showed that fines (silts and clays) made most of the sediments with sand being present mostly at the bottom of the tanks. Loss on ignition data showed that the carbon content did not vary considerably between the layers but varied between sites with the highest concentration at Belper followed by Titford and Horseleyfields.

The SEM results also showed that the organic matter was ubiquitous in the sediments either attached to the sediment matrix or as a coating.

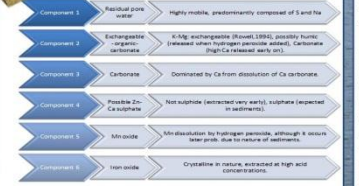




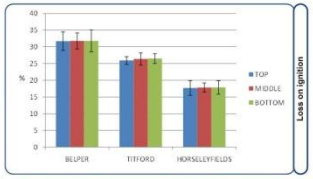
The IC results showed that sulphate concentrations were higher in the supernatant and top layers compared to the middle and bottom layers as expected(Maes, 2003). They were also higher in Belper compared to the other two sites.

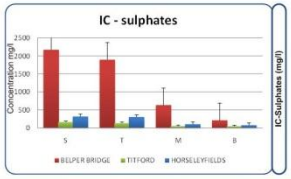


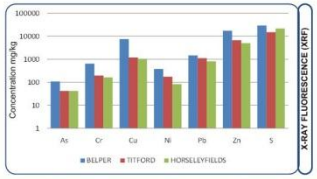
The diagram below shows the XRF results for the 6 main PHEs and sulphur. The concentrations vary from 40-30000 mg/kg for the different elements and are higher at Belper compared to the other two sites.

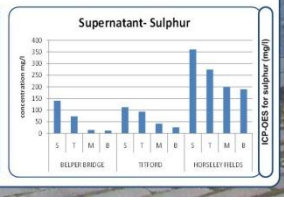


Sulphur content was highest in the supernatant followed by the top, middle and bottom layers with the highest concentrations at Horseleyfields followed by Titford and Belper.





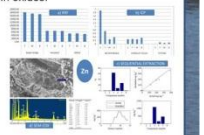




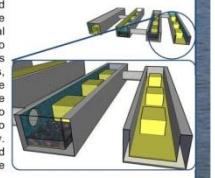
DISCUSSION & REMEDIATION

The results from the various analyses demonstrated that the different sites have different signatures and from the sequential extraction data, it can be deduced that most of the elements are associated with components 2,5 and 6 mainly which are the organic and Fe-Mn oxides.

Various elements are also associated with sulphates in the sediments and this is further supported by IC data. The data has been put together to model the 'behaviour' of the PHEs in the sediments and thus a remediation strategy can be designed accordingly as shown on the figure on the right.



Remediation with zeolites and pulverised fuel ash was the favoured remediation strategy as zeolites have proved to be very efficient for removal of PHEs. Removal efficiency of up to 75% was achieved during pilot trials experiments. 3 types of zeolites, clinoptilolite, chabazite and phillipsite were used in textile mats which can be re-used. Experiments have also shown that they can be reused up to 5 times without losing their efficiency. This method can then be implemented into wetland systems as shown on the right.



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Physical and geo-chemical characterisation of canal sediments modelling of heavy metals behaviour & potential remediation using zeolites and PFAs

- Canals were an important part of the industrial revolution.
- Used mainly for transport of raw materials and end-product.

- Shifted from transportational purposes to more recreational, such as, cycling, walking, fishing.
- Major regeneration and development sites along the canals such as the BCN docks & Olympic games.

Issues:

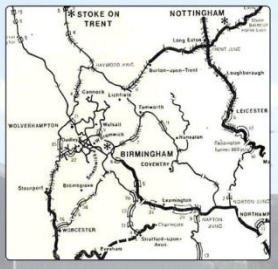
- Heavy metals have accumulated in sediments, which acted like sinks over decades.
- These stay locked up in the sediments until canals are dredged for navigability purposes.
- Wide range of heavy metals present, depending on type of industry surrounding canal location.
- Sometimes at concentrations over guideline values.
- When dredged, sediments can be considered liquid and thus hazardous implying high costs for British Waterways (Landfill and transport costs).
- Little is known about sediments and heavy metal behaviour: research tend to focus on specific heavy metals (lead, cadmium, arsenic, mercury) or specific sites (near high traffic flux) ,(Kelderman *et al.*, 2000, Bijlsma *et al.*, 1996).
- Remediation pilot experiments showed that there was a considerable mass balance difference between heavy metals lost from the sediments and concentration absorbed by zeolites.
- Characterisation thus becoming increasingly important to design the right and efficient remediation strategy.

Characterisation:

Characterisation is crucial when considering remediation of canal sediments. Preliminary results have shown that there are discrepancies regarding the movement and bioavailability of the heavy metals. Preliminary results from the feasibility tests showed that there was a mass balance difference after the zeolites treatment (heavy metals concentrations lost from sediments did not match percentage concentrations adsorbed onto zeolites). This could be due to several factors, for example, heavy metals being oxidised and bound to pyrite or other compounds in the oxidising layer. It is thus very important to understand and map every movement, state and form of the heavy metals during the process. There is a gradual or sometimes sudden change in their behaviour from when the sediments are dredged to the point when they settle after collection.

Site description:

The canals chosen for this research are all in the West Midlands region. The preliminary samples were taken from Belper Bridge found on the Wednesbury old canal which is a connection from the Walsall canal to the Birmingham canal main line. The second sampling site was at Titford canal in Oldbury. This canal is well known for the high concentrations of heavy metals and especially high concentration of organic matter. The third sampling site is Horseleyfields Bridge near Wolverhampton city centre. This site was also an area of high industrial significance and thus has accumulated heavy metals over the years.



Physical analysis:

- **Redox and pH**

pH and redox were measured in situ at different depths (from base to oxidising layer) in the sediment tanks to measure variations using a standard pH and redox probe. Other methods to measure pH and redox such as shaking sediment samples with deionised water and centrifuging would not have been effective as the pH and redox potential would have changed with oxygen availability.

- **Particle Size (Malvern Mastersizer)**

Particle size for sediment samples were measured using a Mastersizer. The latter uses a laser dispersion to measure accurately the range of particle sizes in a particular sample. A statistical breakdown of the various component sizes in the sample (percentage of clay, silt and sand) can thus be determined.

Microscopic analysis

This was used as a proxy to further understand the processes occurring in canal sediments. SEM-EDX (Scanning Electron Microscopy- Energy dispersive x-ray) was performed on samples from the oxidising, middle and bottom layers. Samples were gold coated when required for imaging purposes. SEM-WDX (wavelength dispersive x-ray) was used to map elements to show whether the elements are absorbed, adsorbed or attached to particles or compounds in the matrix. Mapping on EDX did not provide accurate results for elements at low concentrations.

Geo-chemical analysis:

- **Elemental and ionic concentration in pore water**

Cores were taken out and sectioned into three (top, middle and bottom) and centrifuged. The supernatant was filtered and analysed using inductively coupled plasma (ICP) for elemental concentrations. The aforementioned methodology was also undertaken for ion chromatography analysis (IC) for ions such as sulphates, chlorides, sulphides, phosphates and nitrates.

- **Elemental concentrations in sediment**

Ten PVC cores were inserted at random locations in the sediment tank. The tank was then frozen at -20 degrees Celsius. Once frozen, the cores were chiselled out of the structure and were sectioned (top, middle and bottom). These were dried, crushed, sieved and pressed into discs for XRF and XRD analysis.

- **Sequential extraction**

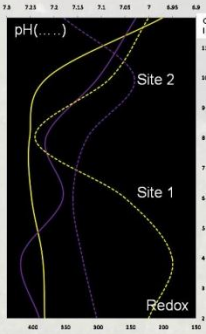
The sequential extraction procedure used for this research, which was developed by the British geological survey (BGS), involved a simple separation technique using nitric acid at various molar concentrations. The samples from the three sections were inserted into centrifuge tube pre-filters (Vectaspin Anopore 20) and centrifuged with the nitric acid. The supernatant was analysed using ICP and the results were examined using a BGS software to map the various fractions in the sediments.

- **Organic loss on ignition**

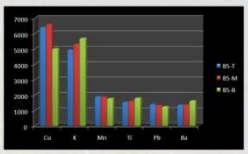
The samples were dried at 40 °C in crucibles and then weighed. They were then transferred to the oven pre-heated at 500 °C for two hours. They were left to cool down and were placed in a decicator to remove all the moisture they absorbed during the cooling down period. Finally, they were weighed again to find the dry weight after burning.

Results:

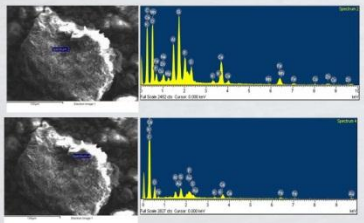
The preliminary results showed that Redox and pH were variable in the sediments as expected. The sediments remained reduced in the tank even after long periods of time. The first site samples were kept for 2-3 months before being analysed. The second sample site was analysed as soon as they were collected. The graph below shows the pH and redox for the two sites.



The ICP results showed a common pattern in elemental distribution throughout the sediment profile. This will help in characterising heavy metal distribution especially regarding binding to specific elements such as iron and manganese. The IC results have shown that there was a very high concentration of sulphates in the sediments and especially in the top layer and in the supernatant.



XRF results for top, middle and bottom layers have also exhibited similar elemental distribution with some minor anomalies which could be due to point specific pollution cases. The elemental distribution will help devise a model of heavy metal distribution in the sediment matrix which in turn will help in designing the most efficient remediation strategy.



The SEM-EDX has shown that there is an agglomeration of the elements in the matrix. The elements were either attached to or were being coated by the organic matter.

Further work:

GC-MS will help in determining whether most of the heavy metals are actually in the organic phase. SEM-WDX will be used to map the elements so that the most appropriate remediation strategy can be developed. The final stage of the characterisation will utilise sequential extraction giving a better overview of the distribution of the heavy metals in the sediments.

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